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(54) Titre : UTILISATION DE COMPOSES TENSIO-ACTIFS A BASE DE GLYCOSIDE ALKYLE DANS DES FLUIDES DE FORAGE A BASE D'EAU ET D'HUILE ET AUTRES AGENTS DE TRAITEMENT POUR Puits DE FORAGE
(54) Title: USE OF SURFACE-ACTIVE ALKYL GLYCOSIDE COMPOUNDS IN WATER- AND OIL-BASED DRILLING FLUIDS AND OTHER DRILL-HOLE TREATMENT AGENTS

(57) Abrégé/Abstract:

Described is the use of surface-active alkyl glycoside compounds as ecologically compatible emulsifiers of the W/O type and O/W type, respectively, in fluid and pumpable drilling fluids and other fluid drilling-hole treatment agents which comprise a continuous or a dispersed oil phase together with an aqueous phase and which are suitable for an environmentally acceptable exploitation of geological resources, for example oil or natural gas deposits. The invention further relates to inverted drilling fluids which are suitable for a non-polluting exploitation of geological resources and contain a continuous oil phase and, present therein, a dispersed aqueous phase together with emulsifiers, further conventional auxiliary agents such as thickeners, fluid-loss additives, weighting agents, water-soluble salts and/or alkali reserves, said inverted drilling fluids being characterized in that they contain surface-active alkyl glycoside compounds of formula (I) as emulsifier or as an emulsifier component together with an ecologically compatible continuous oil phase.

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Abstract of the Disclosure

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The invention further relates to inverted drilling fluids which are suitable for a non-polluting exploitation of geological resources and contain a continuous oil phase and, present therein, a dispersed aqueous phase together with emulsifiers, further conventional auxiliary agents such as thickeners, fluid-loss additives, weighting agents, water-soluble salts and/or alkali reserves, said inverted drilling fluids being characterized in that they contain surface-active alkyl glycoside compounds of formula (I) as emulsifier or as an emulsifier component together with an ecologically compatible continuous oil phase.

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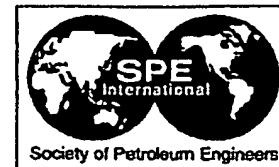
Asserted Claim 149

(depends from Asserted Claim 5)

Element	References	Location of Element in Each Reference
149. The fluid of claim 5 wherein said fluid is used in drilling a borehole in a subterranean formation such that there is a reduction in the loss of drilling fluid into said subterranean formation.	(A) (B) (J) (L) (N) (P)	p. 3 col. 1 RM-63 brochure p. 1; See Reference I pp. 42; 199-200 p. 2 ll. 23-24; p. 8 ll. 7-10 p. 3 at col. 2 ll. 23-26 p. 5 at col. 2 ll. 7-29 pp. 7, 12; See Reference I pp. 42; 199-200

¹ The preamble is not a claim element. Even if the preamble is a claim element, "fragile gel" characteristics and behaviors are inherent in the drilling fluids comprising elements (a) through (d) of each and every asserted claim. See, e.g., the following references:

- (A) p. 2 col. 1; p. 2 col. 2 to p. 3 col. 1; p. 3 cols. 1-2; p. 4 col. 1
- (B) RM-63 brochure p. 1
- (H) p. 365 col. 2; p. 366 col. 1; p. 367 col. 2; p. 368 col. 1
- (L) p. 1 col. 2
- (N) p. 6 col. 1
- (P) p. 7, 12; See Reference (B) above
- (Q) HAL_0015054-55



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New Low Viscosity Ester Is Suitable for Drilling Fluids in Deepwater Applications

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Abstract

High biodegradability and relatively low toxicity have long made esters universally recognized as the best base fluids for synthetic-based muds in regards to environmental performance. A major limiting factor in the use of ester-based fluids, particularly in deep water, is the inherently high kinematic viscosity, a condition that is magnified in the cold temperatures encountered in deepwater risers. These higher viscosities are believed to be especially critical in deepwater wells where lack of overburden causes a severely narrowed window between pore pressures and fracture gradients. Other implications of these higher viscosities include limitations on oil/water ratios, mud weights, and drill solids tolerance.

A new low viscosity (LV) ester has been developed which overcomes these limitations while maintaining the significant environmental advantages of the original esters. The new LV ester has a kinematic viscosity nearly equal to that of currently used internal olefins. It allows formulations of drilling fluids that can be used effectively in virtually all drilling applications in the Gulf of Mexico (GOM), including deep water.

The GOM test protocol was developed to prove the viability of the LV ester as a base fluid. This protocol was designed to consider all conditions drilling fluids are expected to encounter during the course of a well. It evaluates the temperature stability, low temperature rheological properties, and the contamination tolerance of drilling fluids formulated with an LV ester base fluid. Three LV ester fluids were subjected to this protocol: an 11.0 ppg mud; a 14.0 ppg mud; and a 16.0 ppg mud. Results from this extensive laboratory testing indicate new LV ester-based fluids have overcome previous limitations, exhibiting exceptional cold temperature rheological properties, the ability to use a wide range of mud weights and oil/water ratios, and a high tolerance to

contamination. In July 2000, an LV ester-based drilling fluid was used to drill a 3651 ft. interval of a GOM well in 3,669 ft. of water. The LV ester fluid performed well in comparison to the same interval drilled on an offset well with an internal olefin fluid. The initial results from that field trial are included in this paper.

Development of Esters

In 1985, development began on a fully biodegradable base fluid at the request of operators facing restrictions on the use of and discharges from conventional oil base fluids. Esters were found to be the most suitable naturally derived base fluids in terms of potential for use in drilling fluids, being exceptional lubricants, and showing low toxicity and a high degree of both aerobic and anaerobic biodegradability. Ester fluid provides similar shale stabilization and superior lubricity to mineral oil-based mud, and yet also satisfies environmental parameters.

The first trial of the conventional ester-based fluid in February 1990, took place in Norwegian waters and was a technical and economic success. Since then, nearly 400 wells have been drilled worldwide using this C₁₂-C₁₄ ester-based system (Table 1).

The release of ester-based fluids into the global drilling fluids market initiated the era of synthetic-based invert drilling fluids. Following the success of esters, other drilling fluids classed as synthetics were formulated, but these synthetics have not matched the environmental performance of ester-based drilling fluids. One of the most important criteria that they have failed to meet is that of biodegradability; additionally, some have been rejected as a result of poor ecotoxicological or technical performance.

Drivers for Low Viscosity Ester

A low viscosity base fluid was required to give operators the choice of using a system that fulfils more technically demanding requirements than existing ester-based systems, with a particular value in the deeper, colder environments increasingly explored today. The conventional ester is a C₁₂-C₁₄ ester manufactured from palm oil. Research demonstrates that C₈ esters have lower viscosities than their conventional equivalents over a wide temperature range. This led to the development of a lower viscosity C₈ ester base fluid.

Esters have fallen into disuse due to the perception that the elevated viscosities they exhibit at cold temperatures

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contribute significantly to excessive equivalent circulating densities (ECDs), causing an increased risk of lost circulation. This is particularly observed in deep water where long riser lengths are required. The development of an LV ester-based fluid was required to give operators a choice that combines good technical performance with environmental benefits.

Low Viscosity Ester Advantages

Shorter chain length, low viscosity C_8 esters have been developed in response to the increasing importance of viscosity issues as operators move into deeper waters. The viscosity of this fluid is similar to or less than that of other synthetics employed in the Gulf of Mexico.

This offers the following technical advantages:

- Can be used to formulate muds that are stable to 300°F
- Can be used to formulate muds to 16.0+ ppg mud weight
- Can reduce ester/water ratios to 70/30, thus reducing volumes of base fluid discharged
- High tolerance to drilled solids
- Flat gels make it easier to break circulation, minimizing initial circulating pressures and subsequent risk of fracture
- High tolerance to seawater contamination
- Rheological properties can be adjusted by use of additives to suit specific conditions

Substantial testing of this fluid was carried out using a testing protocol designed to simulate conditions to which a fluid may be exposed, including evaluation of temperature stability, low temperature rheological properties, and tolerance to contamination.

LV C_8 Ester Performance

Typically in the GOM, mud is mixed in a mud plant, transported to the rig, and then circulated. While drilling, the mud is exposed to higher temperatures as drilling depth increases. The mud is static in the hole during logging and trips. The fluid must be able to tolerate drill solids and water influxes that may be experienced during drilling operations. In addition, for safety reasons, the drilling fluids must be stable to at least 2.0 lb/gal above the drilling density. The test protocol was developed to simulate and test the effects of those conditions on the LV ester-based fluid.

Three LV ester fluids were subjected to the protocol: an 11.0 ppg mud; a 14.0 ppg mud; and a 16.0 ppg mud. These weights are typical of those used in the GOM. Tests were also run on a 17.0 ppg C_8 LV ester fluid to ensure that the fluid would perform at higher than normal densities.

Temperature Stability. The three muds showed temperature stability from 40°F (4°C) to over 300°F (148°C). This temperature range encompasses the vast majority of operations in the GOM. Fann 75, high pressure and temperature rheological data, indicated yield points of 6, 8, and 8 lb/100ft² at 300°F for the 11.0 ppg, 14.0 ppg, and 16.0 ppg fluid, respectively (Figure 1). These fluids also provide adequate

low end values (6 and 3 rpm) to support suspension of cuttings while maintaining yield points of 50 lb/100ft² or less at 40°F (4°C).

Ester-based fluids should not be used to drill wells that reach temperatures greater than 320°F (165°C). However, fewer than 10% of the wells in Gulf of Mexico are predicted to have temperatures exceeding 320°F (165°C). The majority of these wells are located on the shelf where shipping of cuttings to shore can be readily carried out, or is already necessary due to coastal discharge restrictions.

Mud Density. The use of mud weights exceeding 15.0 ppg for current deepwater applications is rare; however it is possible that higher mud weights will be required. Low viscosity C_8 ester fluids have been successfully formulated to 17.0 ppg (Figure 2).

Ester/Water Ratios. For the GOM protocol, 16.0 ppg and 17.0 ppg LV C_8 ester fluids were formulated and tested with an 80/20 ester/water ratio (EWR). A conventional C_{12} - C_{14} ester-based system would require a 90/10 EWR at these densities due to base fluid viscosity. Flexibility in EWR choices enables the fluid to tolerate water contamination with fewer detrimental effects.

There is also an economic advantage. Based on the amount of oil required per barrel of mud, utilizing a 70/30 EWR versus an 80/20 EWR in an 11.0 ppg fluid reduces the base oil requirement by 12.4% (Figure 3). The cost per barrel is reduced proportionally, and less ester is discharged on cuttings, giving an environmental benefit.

Tolerance to Drill Solids Contamination. The API recommends simulated solids stressing of drilling fluids at a concentration of 35 lb/bbl for mud weights below 15.0 ppg and 20 lb/bbl for muds above 15.0 ppg (API RP13 I, Section 24.6). The GOM protocol solids stressed the muds at concentrations of 20 lb/bbl and 40 lb/bbl. In all three mud weights tested, there were no significant effects on fluid properties. The 14.0 ppg fluid was tested with up to 80 lb/bbl of solids contamination with no detrimental effect on rheological properties. The effects of solids on yield points at 120°F are represented (Figures 4-6).

Cold Temperature Rheological Properties. One of the limitations of the conventional C_{12} - C_{14} ester systems was a high viscosity at temperatures below 40°F. Using the same formulations, the 600 and 300 rpm Fann 75 dial readings are significantly lower for the LV C_8 ester, in comparison to the C_{12} - C_{14} conventional ester (Figure 7).

Using the same testing protocol, the LV C_8 ester fluids demonstrate rheological properties similar to the internal olefin fluids currently being used in deepwater GOM (Table 2).

Breaking circulation. During certain operations, the mud will be static in the wellbore for extended periods. Previous C_{12} - C_{14} ester-based systems became thick, increasing the

pressure required to break circulation. Low viscosity ester fluids do not demonstrate a time-dependent thixotropic behavior, reducing the pressure required to break circulation. The LV C₈ esters exhibit flat gels requiring reduced pressure to re-establish circulation. This helps prevent lost circulation due to fracturing (Figures 8-9).

Seawater Contamination. Testing indicated little change to the yield point values with the addition of 10% seawater to the 11.0 ppg and 14.0 ppg LV ester fluids. At 16.0 ppg, the seawater contamination caused an increase in yield point, as expected, but not unlike what would be found with other synthetic fluids (Figure 10).

First Field Test of LV Ester-Based Fluid

A field test of a low viscosity ester-based fluid took place in July 2000 at a deepwater location in the Gulf of Mexico. The well was situated in 3,669 ft. of water. The LV ester-based fluid was used to drill a 17-in. interval from 5,137 – 8,788 ft MD. The performance of the LV ester-based fluid was compared with the performance of a C₁₆/C₁₈ internal olefin fluid used on an offset well drilled by the same operator in the same block. The results of this comparison are provided graphically (Figures 11-14).

Downhole pressures were measured using a Pressure While Drilling (PWD) tool. This is the most effective way in which pressure-related data can be gathered in the well, and in real-time. One of the points of contention with the original ester was the perception that the elevated viscosity in the riser caused abnormally high ECDs, but the real-time PWD data show otherwise. The pressures generated while drilling and under static conditions with the LV ester-based fluid were similar to those generated with the internal olefin fluid (Figures 11-12). The 17-in. intervals on both wells were drilled at similar rates of penetration.

Yield Point. The yield point of the system can be changed. This is important in start-up of circulation which has been identified as the cause of problems such as lost circulation associated with the conventional ester based systems.

New thinning agents have been developed specifically for the LV ester-based system. These products contribute significantly to the performance described here. As measured under ambient conditions at 80°F, after treatment with thinners the yield point on the field test well dropped from 60 lb/100ft² shortly after drilling began to a final yield point of 10 lb/100ft² prior to running casing (Figure 13). 14

These new thinners are also effective with conventional ester-based fluid systems, thereby increasing the viability of such systems in deepwater environments, where many operators have conventionally considered the viscosities while initiating circulation to be prohibitively high.

Gel Strengths. At 120°F, the LV ester fluid properties reflect the effectiveness of the new thinners. The gels are basically

flat, and the 10-second and 10-minute readings drop significantly after the fluid is treated with thinners (Figure 14). 13

LC50 Results. In the 96 hour Mysid shrimp test, the system exhibited excellent LC-50 results for a newly built, lightweight synthetic fluid. The 9.2 ppg non-sheared plant sample had an initial value of 292,700 mg/L. Shearing typically increases the LC50 value, as was the case on the field test. After the interval had been drilled, the LC50 value for the 10.1 ppg LV ester-based fluid was 432,600 mg/L.

Environmental Properties of Esters

As a class, esters have always been recognized for providing the best environmental performance of any synthetic based fluid. Test data demonstrates that the new LV ester exhibits all the advantages typically associated with esters.¹

Aerobic and Anaerobic Biodegradation Testing. The simplest test method is to place the fluid in an aerobic environment and allow the fluids to degrade for a period of time. The extent to which degradation takes place can then be measured.

A better indicator of the extent of degradation expected in the field is the anaerobic biodegradation test. When base fluids become buried in cuttings piles, the available oxygen very quickly falls to zero. As a result degradation is best measured in such anaerobic conditions. Typically, internal olefin degradation under anaerobic conditions as measured by the ECETOC test is 42%, half of that typically measured for both conventional and low viscosity esters (Table 3).^{ii,iii} However, aerobic degradation is measured at similar rates for internal olefin and esters in the BODIS aerobic biodegradation test.^{iv}

Solid Phase Biodegradation Testing. In tests run by the USA EPA, conventional C₁₂-C₁₄ ester showed significantly greater degradation than all of the other drilling fluids tested. In contrast internal olefin results could not be easily discerned from other fluids.^v

In concurrent tests completed by the same laboratory, low viscosity C₈ ester showed patterns of degradation similar to those of the conventional ester (Figure 15).

Closed Bottle Testing. The anaerobic closed bottle test indicated one primary result: only ester based drilling fluids biodegrade significantly in a reasonable timespan. It has been suggested that other fluids tested were in a lag phase for periods of up to and including 160 days.⁵ However, if such fluids do not biodegrade in ideal conditions in the laboratory (68°F/20°C) in such a timespan, it is not expected that they will degrade well in colder, anaerobic conditions in the field.

Respirometry. This test indicated that conventional esters degrade significantly better than the other drilling fluids tested.⁵ Esters showed significantly different degradation from diesel, whereas the other drilling fluids did not.

Toxicity Testing

The toxicities of both LV and conventional ester-based fluids are very low, when tested using both U.S. and European test species (Figure 16). For the US *Leptocheirus* 96-hr LC50 test,

which is currently under development, a suite of base fluids was tested simultaneously with the low viscosity C₈ ester and conventional ester so that a comparison of resulting data could be made.

Leptocheirus Testing: 96-Hour. Tests were carried out by an independent laboratory using EPA recommended methods. Note that both ester base fluids are much less toxic than other conventional base fluids (Figure 14).

Leptocheirus Testing: 10-day. A series of representative base fluids and whole muds were run in the 96-hour and 10-day Solid Phase Toxicity test by industry. Again, esters showed superior performance (Tables 4-5).

Seabed Surveys

Seabed surveys taken after the discharge of cuttings from any synthetic-based drilling fluid indicate that there is a smothering effect on the seafloor as the result of deposition of cuttings. As soon as any organic matter present begins to biodegrade, the levels of oxygen are reduced. This has an effect on benthic communities.

However, the biodegradation of esters continues in the absence of oxygen. Cuttings are hydrated and dispersed, aerobic conditions are re-established, and re-colonization by benthic infaunal individuals occurs. The animal communities recover shortly after discharges have ceased.

One year after drilling with an ester-based fluid ceases, subsequent surveys indicate seabed recovery, reflected in species diversity and number, and also in total abundance of individuals.^{vi}

Apart from the rapid recovery of the benthic community, all surveys have shown that the levels of ester in the sediment were below 5,000 ppm in most cases; these were greatly reduced within one year, and two years after drilling, the levels were all but undetectable. Similar patterns of recovery are expected with the LV ester.

Conclusions

The new low viscosity ester-based fluid overcomes all technical criticisms of conventional esters while maintaining the environmental advantages that the systems have always provided.

- The C₈ ester performed well when tested using a protocol designed specifically to simulate GOM conditions.
- When field tested on a GOM well in 3,669 ft. of water, the LV ester-based fluid demonstrated promising performance. Based on PWD measurements, the ester fluid showed lower ECDs than those observed while drilling a comparable interval with internal olefins on an offset well.
- The biodegradation and toxicity performance of esters is "best in class" among all synthetic based fluids. The C₈ ester achieves similar results in these important environmental measures.

Table 1 – Number of Wells Drilled with Ester-Based Fluids Globally

Country	Number of Wells
US	58
UK	56
Norway	64
Nigeria	159
Mexico	5
Malaysia	4
Holland	1
Brunei	4
Australia	32

Table 2 – Rheological Properties of IO Fluids and LV Ester Fluids

	Internal Olefin C ₁₅ -C ₁₈ Fluid	Low Viscosity C ₈ Ester Fluid
11.0 lb/gal, 70/30 EWR, 40°F (4.4°C)		
Plastic Viscosity, cP	65	68
Yield Point, lb/100ft ²	36	27
Fann 35 600 rpm dial reading	166	163
Fann 35 300 rpm dial reading	101	95
14.0 lb/gal, 70/30 EWR, 40°F (4.4°C)		
Plastic Viscosity, cP	86	87
Yield Point, lb/100ft ²	44	53
Fann 35 600 rpm dial reading	216	227
Fann 35 300 rpm dial reading	130	140
16.0 lb/gal, 80/20 EWR, 40°F (4.4°C)		
Plastic Viscosity, cP	85	111
Yield Point, lb/100ft ²	21	36
Fann 35 600 rpm dial reading	191	258
Fann 35 300 rpm dial reading	106	147

Table 3 – Biodegradation of LV Ester and Conventional Ester in Anaerobic and Aerobic Biodegradation Test Protocols

		Anaerobic Biodegradation ECETOC Test (%)	Aerobic Biodegradation 28d BODIS test (%)
INTERNAL OLEFIN BASE FLUID	Result	35	80
LOW VISCOSITY ESTER BASE FLUID	Result	89	81
CONVENTIONAL ESTER BASE FLUID	Result	82	96

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Table 4 – Industry Comparisons between 4-day and 10-day Leptocheirus Tests: Base Fluids				
Base Fluids	Mean 96 hr LC50 Concentration mg/kg	Mean 10 day LC50 Concentration mg/kg	Difference	% Change in Toxicity
Diesel	781	639.4	141.6	18
BB 250	2631	483	2148	82
IO	10288	2829	7459	73
Conventional Ester	21380	13499	7881	37

Table 5 – Industry Comparisons between 4-day and 10-day Leptocheirus Tests: Whole Muds				
Whole Muds	Mean 96 hr LC50 Concentration ml/kg	Mean 10 day LC50 Concentration ml/kg	Difference	% Change in Toxicity
Diesel	1.055	0.86	0.195	19
BB 250	2.9	1.25	1.65	57
IO	28.3	3.5	24.8	88
Conventional Ester	59.5	11.6	47.9	81

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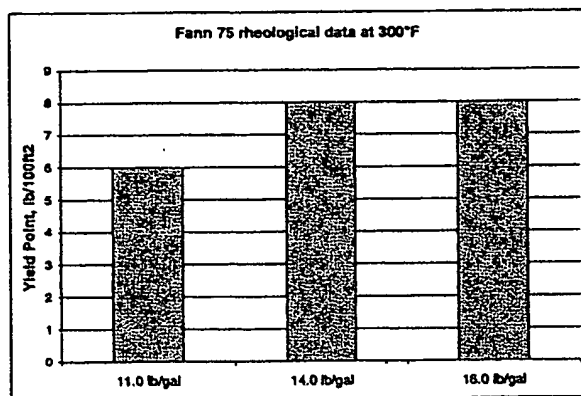


Figure 1 Fann 75 rheological data for low viscosity ester fluid at 300°F.

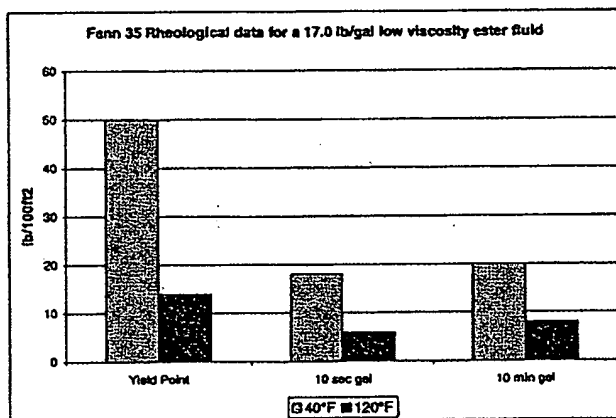


Figure 2 Fann 35 rheological data for 17.0 ppg low viscosity ester fluid.

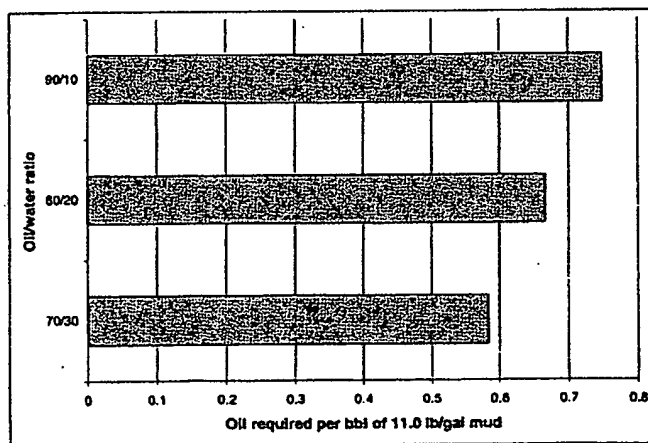


Figure 3 Ester required per bbl of 11.0 ppg mud, varied ester/water ratios.

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Figure 4 Effect of drill solids on 11.0 ppg low viscosity ester-based fluid.
Due to their surfactant nature, the thinners in the formulations do not begin to perform until solids are incorporated.

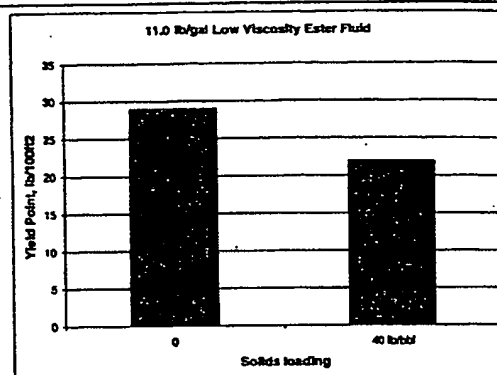


Figure 5 Effect of drill solids on 14.0 ppg low viscosity ester-based fluid.

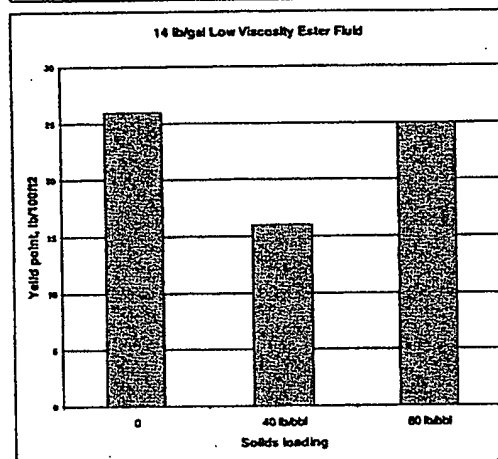
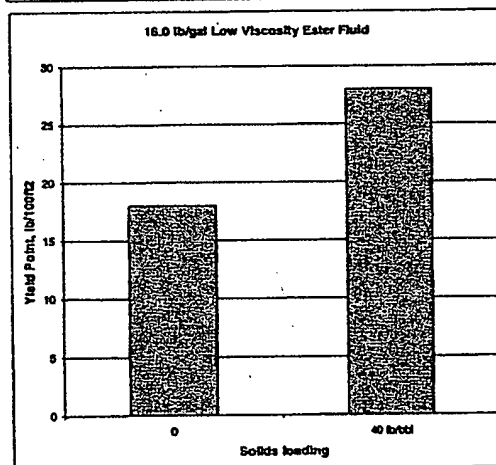


Figure 6 Effect of drill solids on 16.0 ppg low viscosity ester-based fluid.



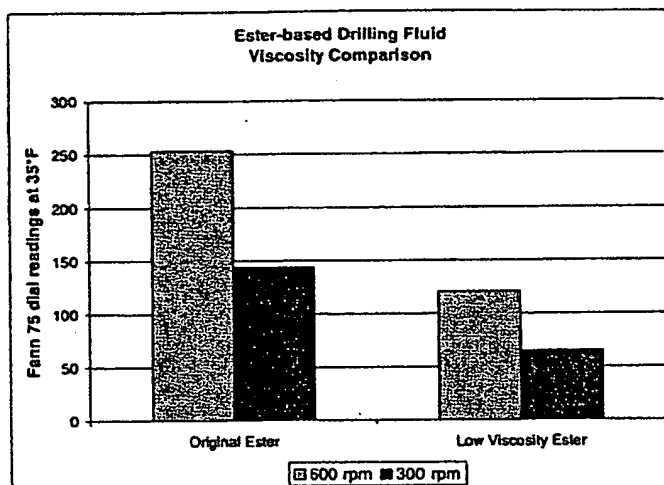


Figure 7 Ester based drilling fluids viscosity comparison.

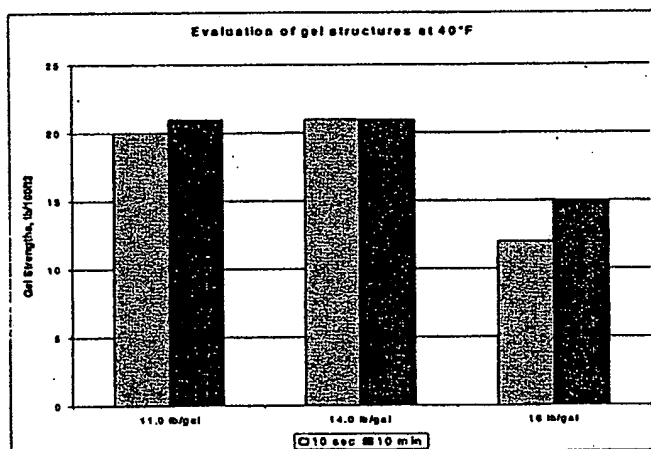


Figure 8 Evaluation of gel structure at 40°F.

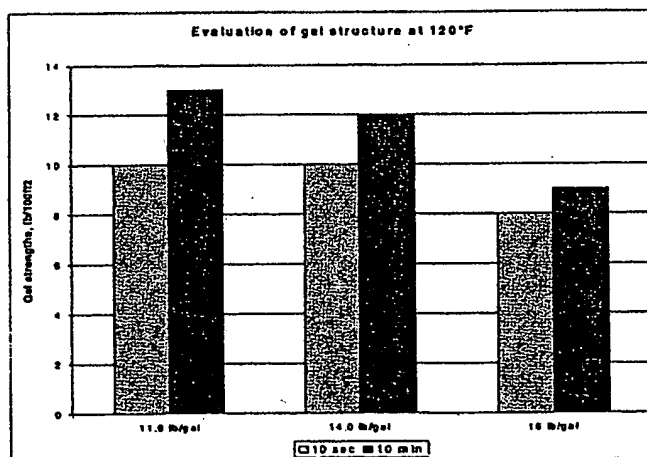


Figure 9 Evaluation of gel structure at 120°F.

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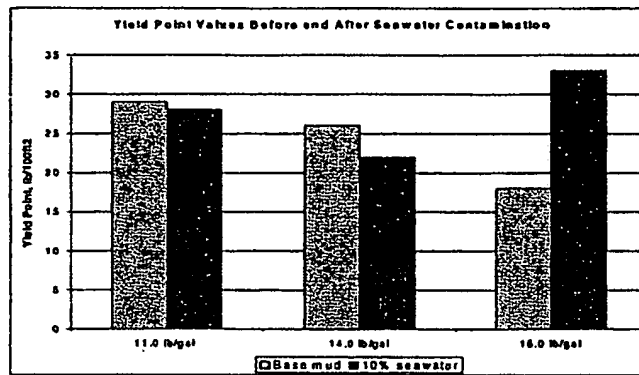


Figure 10 Yield point values before and after contamination.

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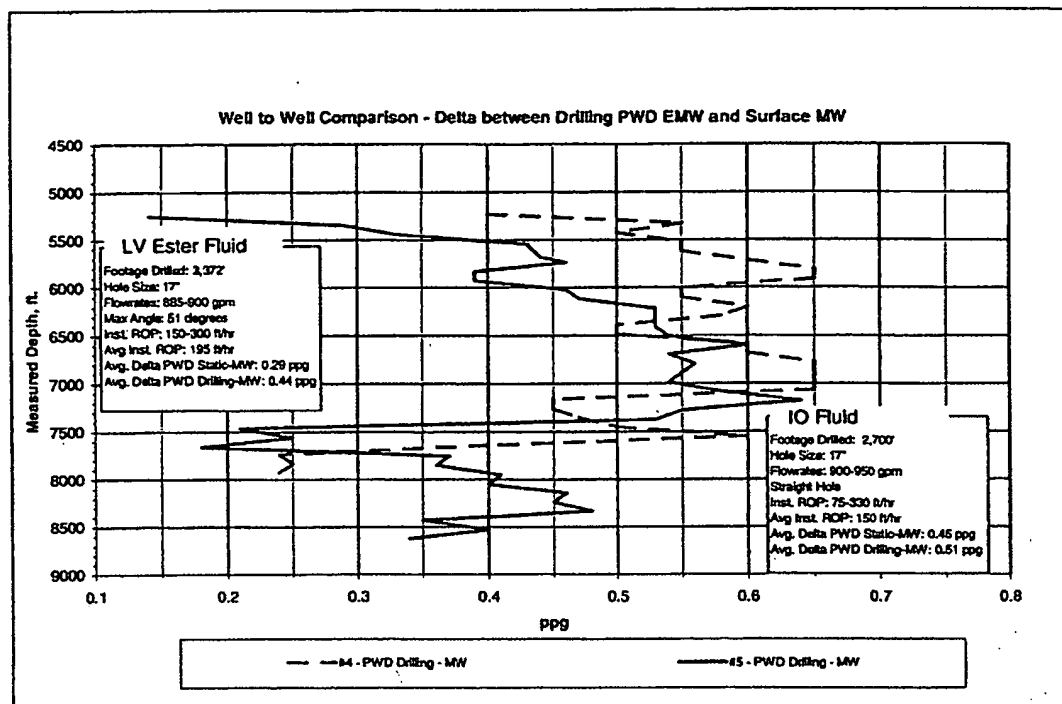


Figure 11 Well-to-well comparison: Delta between drilling PWD equivalent mud weight and surface mud weight.

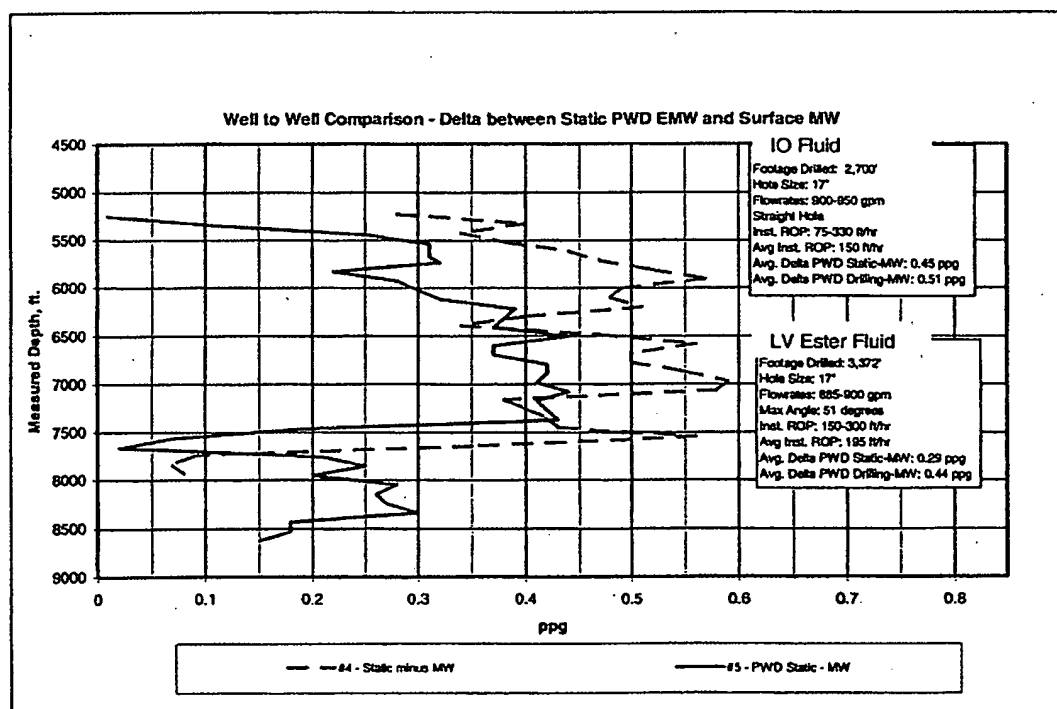


Figure 12 Well-to-well comparison: Delta between static PWD equivalent mud weight and surface mud weight.

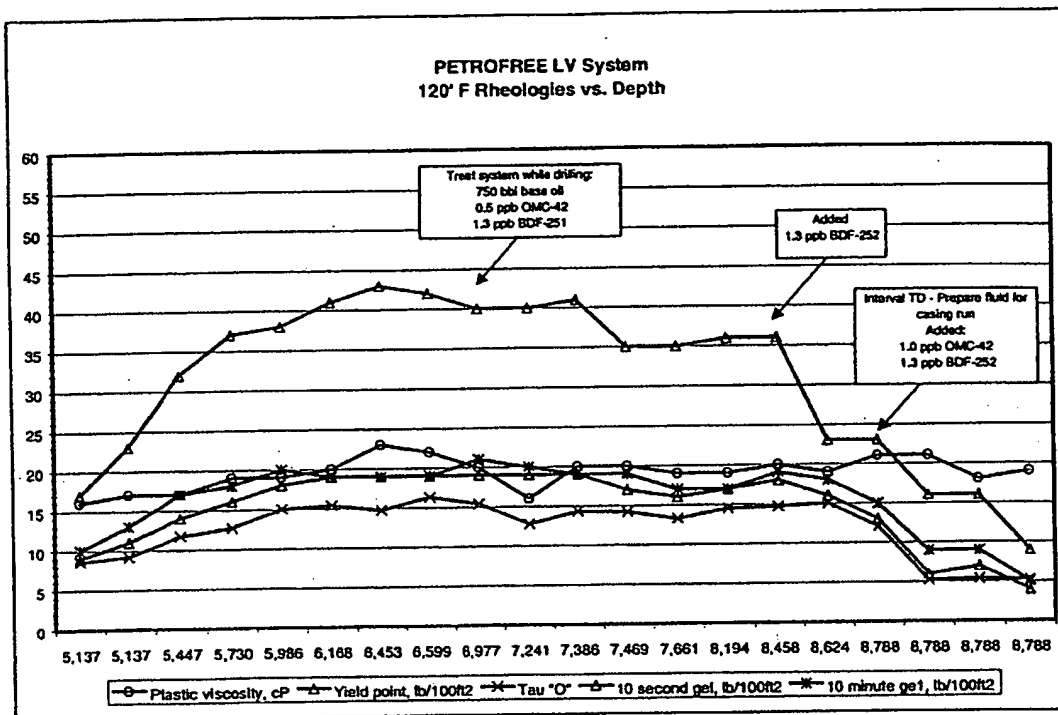


Figure 13 LV ester field test: Ambient rheologies vs. time and depth.

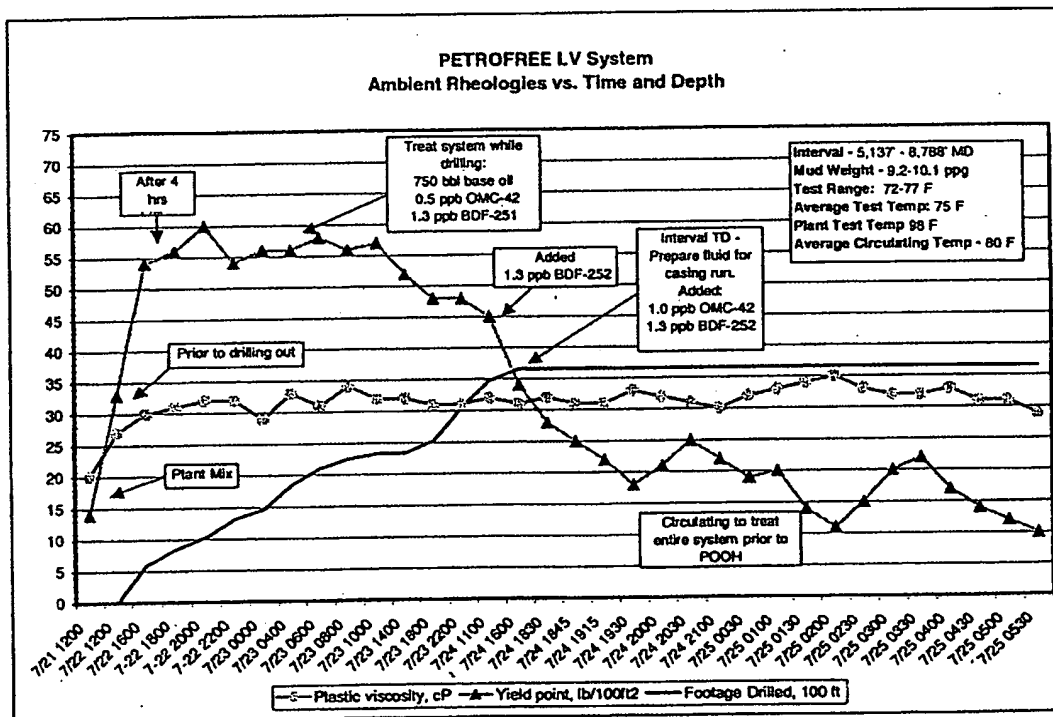


Figure 14 LV ester field test: 120°F rheologies vs. depth.

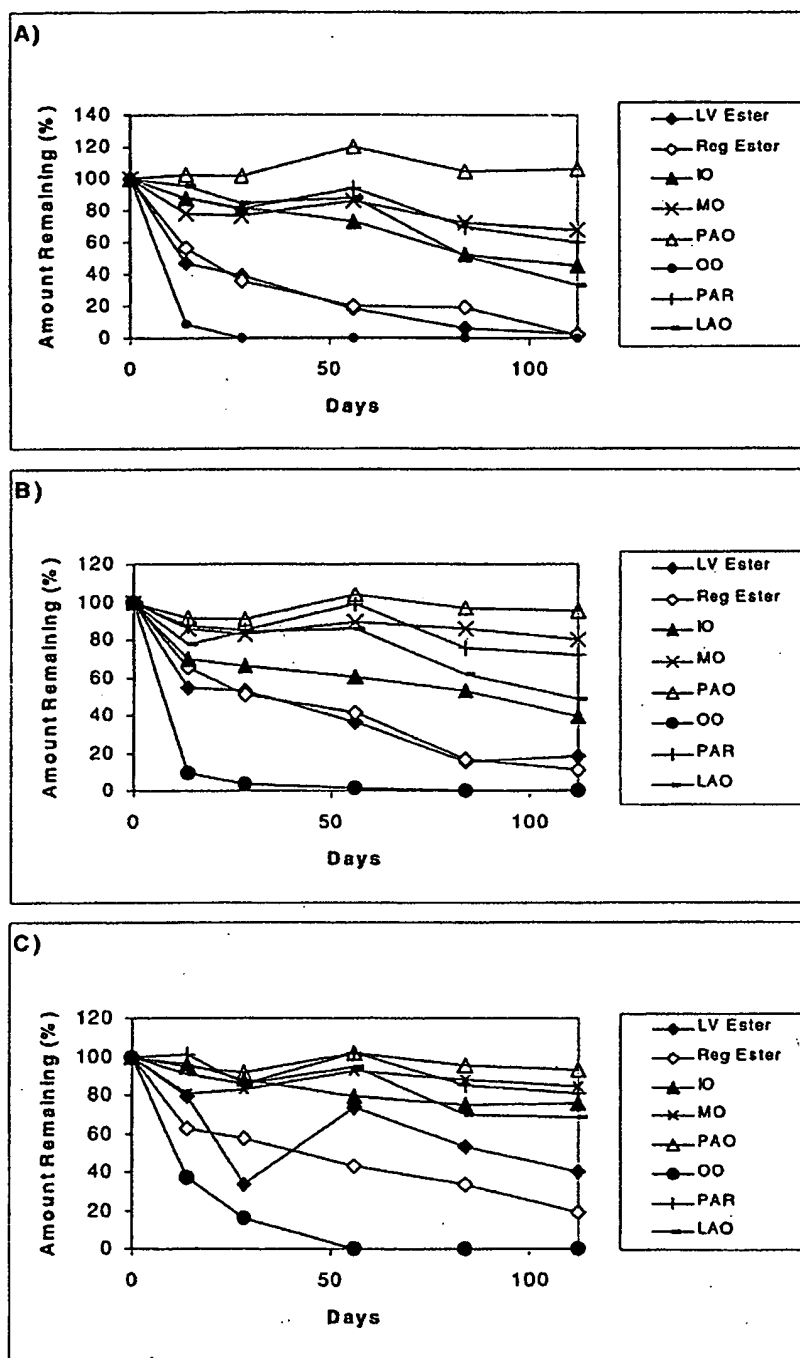


Figure 15 Degradation of esters at 3 different concentrations: a) 1000 ppm; b) 2000 ppm; and c) 5000 ppm.

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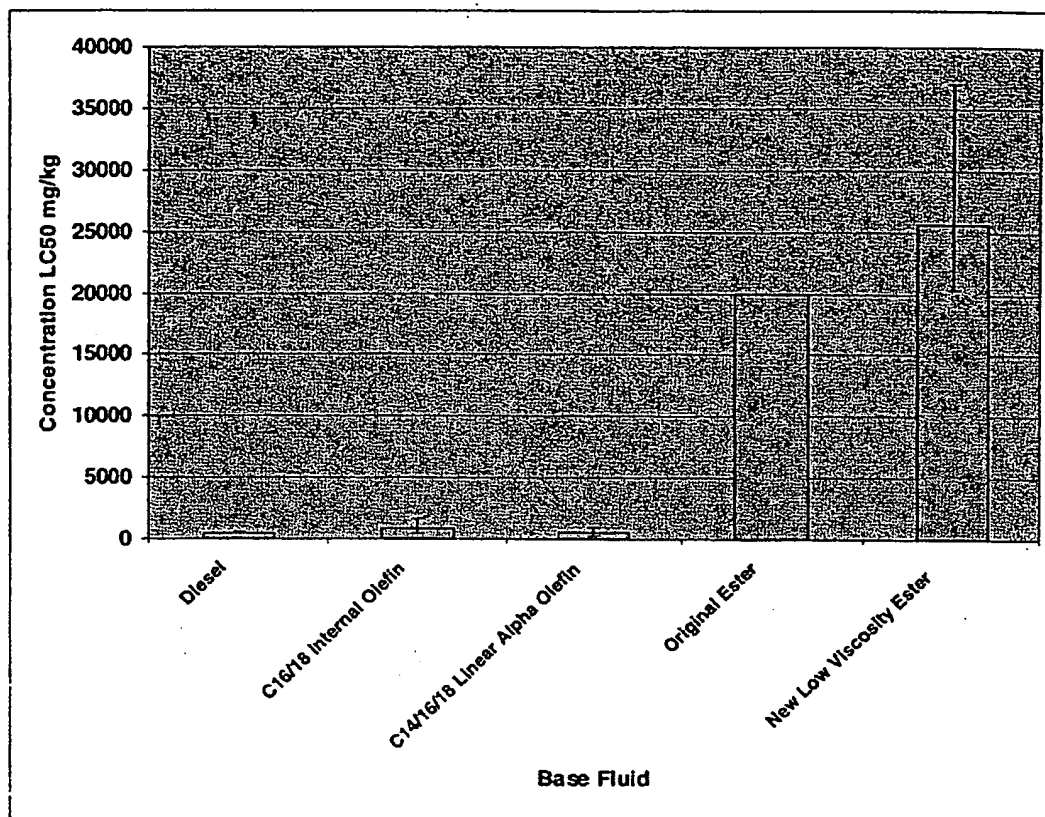


Figure 16 Toxicity performance of esters measured by the 96-hour *Leptocheirus* Solid Phase Toxicity Test in relation to other base fluids commonly used in the US. For the original ester; <50% mortality was observed at a concentration of 20,000 mg/kg, hence no error bar is given as toxicity measured as LC50 is >20,000 mg/kg.

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SPE 65000

High-Density Invert-Emulsion System with Very Low Solids Content to Drill ERD and HPHT Wells

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Abstract

The paper describes the laboratory development of a new Low Solids Oil Based Mud System (OBMS) with a very high specific gravity (2.04 SG; 17 ppg) for high-temperature and high-pressure applications. The system can also be applicable as solid free oil based mud with very low viscosity at densities up to 1.52 SG, especially suggested for Extended Reach Drilling Wells. The main goals of the new system are:

- 1) Optimization of fluid rheology by reduction of the solids contents in the mud.
- 2) Temperature and system stability at 170 °C.

The objectives have been pursued in the following ways:

- by using a very heavy brine as the internal phase;
- by decreasing the oil / brine ratio;
- by using a weighting agent with higher density than barite.

In this way, the amount of weighting solids which needs to be added can be drastically reduced to even below 22% v/v for a 2.04 SG mud, compared to 35% v/v as in traditional oil based muds. Also the PV values have been reduced from typically round 60 cP to even below 25 cP.

The addition of new components to the system has lead to the need of a new emulsifier package, which has been optimized with the development of a primary emulsifier and a wetting agent based on innovative chemistries.

Introduction

Saga Petroleum discovered in 1997 a new high temperature high pressure (HTHP) field offshore Norway, the Kristin field. A total of three exploration wells have been drilled on the Kristin structure. The temperature in the reservoir is 175°C and the pressure 930 bar, requiring the use of drilling fluids with high temperature stability and high density (2.04 kg/l). The drilling of these wells has identified the need of developing a drilling fluid system with better rheological properties and improved temperature stability.

Conventional oil based mud has been used in exploration drilling. In vertical wells the mud has behaved satisfactorily but, when drilling inclined hole, a lot of mud related problems occurred such as barite settling, high equivalent circulating density (ECD) and high surge and swab pressures. To build mud with such high densities, the concentration of weight material needs to be very high. In the wells drilled in the Kristin field the amount of barite was approximately 35% v/v. Together with the drill solids and the organophilic clay, the total amount of solids in the mud was reaching almost 40% v/v. This very high solids content makes it very difficult to achieve a good rheological profile of the mud.

To develop the Kristin field for production several extended reach drilling (ERD) wells need to be drilled. Drilling of these wells cannot be done with this type of mud because of the high ECD, caused by the high rheology of the mud, which might fracture the formation and cause lost circulation problems. The development of a new oil based mud system, which gives far lower ECDs, is therefore essential to be able to drill the necessary wells.

Invert emulsion fluids consist of a salt water solution dispersed into a continuous hydrophobic phase. This emulsion is stabilized by emulsifiers. The salt water phase has traditionally been a CaCl₂-brine, often with lime added for alkalinity. The oil / water ratio is traditionally in the range of 65/45 – 85/15. The concentration of solids in the mud will often dictate the oil / water ratio. In solids laden muds the oil ratio must be high, to keep the solids oil wet and dispersed.

The mud used in the exploration wells of the Kristin field had

an oil / water ratio of 80/20. The water phase used has been CaCl_2 -brine with an S.G. of 1.14. The base oil S.G. was 0.82 and the emulsion S.G. was therefore 0.88. To weight up this emulsion to the desired mud S.G. of 2.04, a total of 35% v/v of barite is needed. The project idea for this new mud system for Kristin has been to reduce the oil / water ratio and to replace the CaCl_2 -brine with a heavier brine. The weight of the emulsion increases and the amount of weighting material needed to achieve the desired mud S.G. is reduced. This heavy emulsion will then be a much better base for building heavy muds with improved rheological properties.

This paper summarizes the findings of the work and suggests a few guidelines for the formulation of a new invert emulsion mud system.

Laboratory Results:

Summary of the work

Three heavy brines have been selected for this study for use as the internal phase in the new mud system:

- CaBr_2 -brine of 1.72 S.G.;
- HCOOK (potassium formate) brine of 1.56 S.G.;
- HCOOCs (cesium formate) of 2.23 S.G.

Muds using formate brines showed to have much better rheological properties than the muds using CaBr_2 -brine; for this reason the results with CaBr_2 -brine are not reported. The CaBr_2 system also seemed to be quite aggressive.

The compatibility between different brines and emulsifiers with different chemistries has been checked, preliminarily by very simple testing (emulsion bottle test), and then confirmed in fully formulated muds.

Compared to the muds previously used in the Kristin field, the oil/brine ratio has been decreased from 80/20 to 60/40 or 50/50. The high brine volume fraction, together with the high salinity of the brines and the surface properties of the selected weighting agent have given quite low electrical stability (ES) values. Nevertheless, stable ES values and low filtrate values have indicated that very good and tight emulsions have been formed. With the optimization of the brine and the oil / brine ratio, the solids content of the mud (S.G. 2.04) has been reduced in some instances to even 18% v/v (50/50 Oil/Cesium formate brine ratio).

In addition, different types of weight materials have been tested: manganese tetraoxide, barite and ilmenite. The tests performed with manganese tetraoxide as weighting agent did not show interesting results because the increased surface area of the solids caused a remarkable increase in mud viscosity. The use of ilmenite as weighting material gave better properties of the mud compared to barite. The improvements from using ilmenite are due to the higher density, because a lower volume of solids needs to be added to the system. In addition, ilmenite has a much narrower particle size distribution, with both less small and less large particles, Figure 1. Small particles have higher surface area per volume

and therefore bind up more fluid, which has a negative effect on the rheology. Ilmenite has also no particles above 40 micron while barite specifications call for 3% maximum of the particles to be larger than 74 micron in diameter. Large particles will sag more easily than small particles, thus ilmenite can have less tendency to sag.

Most of the time has been spent to synthesize and characterize new emulsifiers, because it became clear since the beginning that the emulsifier package needed to be tailored to very demanding conditions (different brines, high densities, surface properties of weighting agents, high temperature). Polyamide based emulsifiers showed the best stability at high temperatures. Increasing the polarity of the emulsifiers gave more stable emulsions. Furthermore, the best combination was to use a primary emulsifier with relatively low hydrophilic/lipophilic balance (HLB) values in combination with a secondary emulsifier (or wetting agent) with higher HLB values. Among all the wetting agents synthesized and tested, the most promising was based on a modified imidazoline.

The optimization of the system has also included the evaluation of two different low toxicity mineral oils (synthetic paraffin A and synthetic paraffin B), the screening of different rheology modifiers/fluid loss reducers and the study on the effects of lime in these invert emulsion formulations.

It has been shown that the HPHT filtrates values were already low and could further be reduced with appropriate fluid loss reducers.

These lab muds have been tested for robustness against contamination such as cement, seawater, drill solids etc. and the samples have also been heat aged at 171°C, both dynamically and statically. Ilmenite settling tests have been conducted.

Muds with a higher density (S.G. = 2.2) or with different oil/brine ratio (80/20) were also formulated and characterized. These new systems have proven to be very robust and flexible to all the above mentioned factors giving good confidence for their successful field use.

Also solids free heavy emulsions were studied, focusing on the rheological properties and emulsion stability.

Very good technical results have been obtained with a system based on the following components:

Continuous phase:	Synthetic paraffin B
Internal phase:	Cesium Formate S.G. 2.23 or Potassium Formate S.G. 1.56
Oil/brine ratio:	60/40
Primary emulsifier:	Emulsifier 2137/3
Wetting agent:	WA 11
Fluid loss reducer:	BF 2745
Source of alkalinity:	lime
Weighting material:	ilmenite

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Tests results with Potassium and Cesium Formate

The Tables 1 and 2 report the rheological behavior of muds with potassium formate, Tables 3 and 4 with cesium formate or with a mixed brine 50/50 potassium formate/cesium formate. The influence of several components/contaminants is also reported. The test results show the flexibility of the system by changing the S.G. or the Oil/Brine ratio. The mud with O/B 80/20 requires a higher amount of ilmenite and this is reflected in a higher requirement of suspending agent to avoid settling. The system show a good flexibility by changing density or by using a mixed brine.

The Components of the System

Mineral Oil

At the beginning of the project it was decided to run all the tests with the same mineral oil: synthetic paraffin A. Synthetic paraffin A is based on synthetic pure paraffins and is one of the mineral oils approved for use in the North Sea (OCNF Group Z Base Fluids) because of its low aromatic content. As the project proceeded, another low toxicity mineral oil has been tested. This oil, called synthetic paraffin B, is also based on synthetic pure paraffins and exhibits lower viscosity than synthetic paraffin A. This parameter is negligible when considering invert emulsion with high oil/brine ratio but, as in our case, where the nature of the emulsion is very crowded, the difference of the base fluid viscosity is mirrored in a better rheological behavior of the mud. The PV value can be reduced by 10-15 cP with synthetic paraffin B as reported in Table 5. Therefore synthetic paraffin B has been considered the preferred mineral oil. Table 6 reports the typical properties of the two oils.

Brine

At the beginning of the work a series of different brines were considered before choosing the base-mud formulation for the evaluation of the emulsifier package. The screening has been concentrated on brines characterized by high density, to reduce the volume fraction of the weighting agent in the mud. In Table 7 the typical properties of the brines taken into consideration are reported.

TKPP (tetrapotassium pyrophosphate), after a first test round, has been cancelled because it reacts with lime: calcium pyrophosphate precipitates and depletes the alkali source in the oil phase. CaCl_2 brine is the most common brine used in invert emulsion systems. This brine was not investigated deeply because of its relatively low S.G. The main focus has been on three brines, the CaBr_2 brine of 1.72 S.G., the potassium formate brine (HCOOK) of 1.56 S.G. and the cesium formate brine (HCOOCs) of 2.23 S.G.

By using CaBr_2 -brine (1.72 S.G.) and reducing the oil / brine ratio to 60/40, the weight of the emulsion is increased to 1.18 S.G. and the amount of barite needed to build 2.04 S.G. mud is reduced to 28% v/v. Ilmenite has a density of 4.6 S.G. as compared to barite 4.2 S.G.; by using ilmenite the amount of

weighting material is further reduced to 25% v/v. The use of cesium formate brine (HCOOCs), which has a S.G. of 2.23 will further increase the weight of the emulsion to 1.38 S.G. for a 60/40 oil / brine system, and the amount of weighting material can be reduced to 21% v/v. In this manner it is possible to build heavy mud with drastically improved rheology. If cesium formate brine is too expensive, potassium formate brine (1.56 S.G.) can be considered, in this case the solids volume will be 27% v/v.

Muds using formate brines showed much better rheological properties than the muds using CaBr_2 brine. The CaBr_2 system also seemed to be quite aggressive. The reason for the better rheological behavior of the formate brines is not fully understood. However, it was noticed that formate brines gave relatively low but stable electrical stability values in comparison with bromides and chlorides. This is probably due to the higher salt concentration in the brine.

Formate brines are becoming more widespread in the last years to make up water based drill-in fluids with low solids content and good clay inhibition. This is also due to their good handling and environmental properties. They are in fact biodegradable, non toxic, not corrosive, very user friendly, temperature stable up to 375°F, compatible with the elastomers (Table 8). They have, however, never been reported field-tested in invert emulsion fluids.

Although their price has decreased in the last years, it is still quite high in comparison with chloride or bromide brines. This is particularly true for cesium formate, although it offers more technical advantages because of its higher density. To reduce the cost a mixed brine 50/50 HCOOK/HCOOCs has been tested. The compatibility between the two brines at all the ratios has been verified with good results. Keeping in mind that these muds can be reconditioned and reused in many wells, the cost per well can be further lowered.

Separate studies conducted by Cabot⁽⁴⁾ and Shell have shown that the solubility of barite in cesium formate was in the range of 600-700 mg/l. The solubility testing clearly shows that in field operations contamination of used cesium salt solutions with barium salts is likely. During this project this problem has been overcome by using ilmenite instead of barite.

Lubricity test results conducted by Cabot with a HLT Lubricity Testing Instrument and a Baroid Lubricity Meter⁽⁴⁾ indicate that both potassium and cesium formate base fluids are extremely lubricious, significantly reducing the coefficient of friction values of metal-to-metal, metal-to-sandstone, and metal-to-shale contact surfaces. The coefficient of friction for formate based fluids was lower than that of mineral oil based invert emulsion fluids based on CaCl_2 brine. Even if formate is the internal phase of the emulsion, it could be argued that invert emulsions formulated with formate brines are very promising to drill extended reach and deviated holes where a low coefficient of friction is needed.

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Weighting Material

For more than 60 years barite has been the main weighting material for muds. There are several reasons for its popularity:

- The high specific gravity (S.G.=4.2) permits weighting the mud with as little increase in solids as practical.
- Its chemical inertness and virtual insolubility in water or oil minimizes effects on mud properties and the environment.
- Barite's intermediate hardness (2.5-3.5 Mohs Scale) is soft enough to prevent serious abrasion of metal but hard enough to prevent excessive attrition and creation of fines.
- It is available in large quantities at low cost to meet the industry requirements of millions of tons per year.

Of all the additives used in the formulation of oil well drilling fluids, the weighting material is used in the largest quantity. Over the past few years iron oxides have come into use as weighting material, such as hematite, ilmenite, itabirite and Fer-O-Bar; among them ilmenite is the most promising. Ilmenite is an iron-titanium oxide and has higher specific gravity than barite and higher hardness (Table 9). During past uses of ilmenite as a weighting agent in WBM, the abrasion on drilling equipment has been of greatest concern because of the harder nature of ilmenite. Many studies have addressed this problem (Geocare, Internal Report, 1997 ⁽⁶⁾ Haaland et al., 1976 ⁽⁷⁾; Blomberg et al., 1984 ⁽³⁾). In general, field observations have been confirmed by laboratory experiments. However, the abrasiveness is highly dependent on the particle size distribution (average and maximum particle size) and experiments clearly show that the abrasiveness of ilmenite can be reduced to that of standard barite by removing the largest particles. It was found (Blomberg et al., 1984 ⁽³⁾) that with less than 3% particles > 45 micron, abrasion could reach acceptable values. Furthermore, ilmenite in oil based drilling fluids showed much lower abrasion.

The ilmenite now available on the market meets this limit. The ilmenite used during this project is produced in South Rogaland, Norway from a hard rock ilmenite ore. The concentrate contains ca. 94% ilmenite with the silicates hypersthene and plagioclase as the main accessory minerals. Ilmenite has lower concentrations of heavy metals such as lead, barium and copper than barite, but is higher in other metals such as chromium and nickel. Studies on flatfish have shown that no metals from ilmenite are bioavailable, although lead, barium and in cases cadmium may be available from barite. Ilmenite is included in the SFT List A of the approved products to be used in the North Sea Norwegian Sector.

The breakdown of barite or other weighting material into smaller particles, can reduce the quality of drilling fluid. The increase of the number of very fine particles results in an increase in the drilling fluids viscosity and reduced penetration rate. If viscosities become too high, the very fine particles must be removed by use of a centrifuge. The particle size distribution of ilmenite (Figure 1), between 6 and 45 micron,

would not results in drilling fluid loss by centrifuge treatment. Because ilmenite is harder than barite, it does not break down to smaller particles as easily as barite. Virtually no attrition will occur for ilmenite during mechanical working, meanwhile barite normally becomes finer grained. During attrition the total number of particles in a drilling fluid may increase to a point where the particles come in contact with each other, and therefore the viscosity of the fluid increases. Attrition by mechanical grinding may result in more rapid increases of yield points and gel strengths for barite containing fluids than for ilmenite containing fluids.

The importance of penetration rates on overall well costs in drilling is widely recognized. If rig time is reduced by higher rates of penetration, overall cost is generally reduced. It is well known from literature (Rupert et al., 1981⁽¹⁶⁾; Blatt et al., 1982⁽²⁾) that the use of ilmenite in drilling fluids (both water based and oil based) can drastically enhance the penetration rate. Based on laboratory and field studies, in fact, the properties of drilling fluids that primarily affect the rate of penetration are viscosity, filtrate loss and solids content. With higher specific gravity weighting material than barite, a lower solids content is needed to obtain the needed drilling fluid S.G. With fewer solids in the system, the particles are allowed to disperse further apart, thus lowering the plastic viscosity. A higher specific gravity weighting material, such as ilmenite, would lead to increased penetration rate, based on its effects on rheology.

Barite is considered partially soluble in formate brines such as those used in this project, therefore it can not be used as weighting material in these kind of fluids. Ilmenite is considered relatively insoluble in formate brines.

In aqueous solutions crystal surfaces are electrically charged. This property determines the state of particle dispersion, rheology of suspensions and whether the particle acts as an absorbent or ion exchanger. The term zeta-potential is used to quantify this property and is considered as the drop in charge across the diffuse layer in an electrolyte. For each particle, the zeta-potential is dependent on the pH and the dissolved ions in the aqueous fluid. Ilmenite displays a zeta-potential pattern typical of oxide minerals with a low zeta-potential at high pH conditions, whereas barite has a more stable zeta-potential. At high pH, such as common for drilling fluids, the surface charge of ilmenite will therefore result in dispersion within the drilling fluid. For barite under similar conditions, particles will not be dispersed and will actually come in contact with each other so that van der Waals' bonding between crystals may occur. Van der Waals' attraction between particles would cause agglomeration of particles and would also affect rheological properties of drilling fluids.

Other advantages of ilmenite as weighting material include solubility in acids, reaction with sour gases, less fine particles, very low attrition rate and no appreciable settling. This result in a stable rheology with limited need for dilutions and

chemical conditioning, therefore allowing lower drilling fluid maintenance costs. Table 10 show the results of the same mud formulated with barite or ilmenite.

Emulsifier Package

The synthesis of the primary emulsifiers was focused on polyamides because this is the chemical class that shows the best stability at high temperatures. Starting from polyamides with known performance in invert emulsion muds at high oil / brine ratio and high temperature, polyamides were synthesized with different molecular weight (MW), hydrophilic-lipophilic balance (HLB), different polarity and fatty acid sources. The starting point polyamides showed high viscosity of the system and / or unstable emulsions when very heavy brines were used. This fact is particularly evident with calcium salts, whereas potassium formate brines gave lower viscosities but with lower electrical stability before and after aging. It was shown that not all the emulsifiers normally used and available on the market are able to tolerate variable oil / brine ratio ranging from 90/10 to 50/50.

All the emulsifiers synthesized have been formulated in a suitable solvent, at the same active content and characterized. The emulsifier concentration has been optimized testing different concentrations (Table 11).

During the project it was realized that also a wetting agent with higher HLB was needed to control the rheology of the system. A separate evaluation has been performed to develop an appropriate wetting agent. A number of surfactants have been synthesized and evaluated with different types of chemistries and hydrophilic/lipophilic properties. The two products that have shown the best behavior were Emulsifier 2137/3 (Primary emulsifier) and WA 11 (Wetting agent).

Lime

Ilmenite reacts with sour gases, such as H_2S , that may be encountered during drilling. Because of that, lime is theoretically not needed in the developed system. Nevertheless some tests have been performed to establish the properties' variation of the base mud by addition of an alkali. Alkaline substances are used to block acidic influxes, such as hydrogen sulfide, carbon dioxide or the products of degradation of organic compounds; in addition, the calcium salts of fatty acids are known to be water in oil emulsifiers. Besides lime, potassium hydroxide was used to verify any possible difference due to the precipitation of calcium formate with lime. The addition of lime has been found to be beneficial to the stability of the emulsion and to the filtrate (Table 13 and 14).

Rheology modifier

Some different rheology modifiers have been screened during the project. Products based on fatty acid polyamides, tall oil dimer acids or synthetic polymers have been tested without interesting results. Rheology modifiers are not required in the system because rheology and suspending properties of the

mud can be adjusted by selecting the right oil / brine ratio and the organoclay concentration. Furthermore, by using heavy brines and a heavy weighting agent the amount of solids to suspend can drastically be reduced. The particular size distribution of ilmenite is such that ilmenite is easier to suspend than barite.

Fluid Loss Reducer

High-pressure high-temperature fluid loss (500 psi, 340°F) has been investigated only once the rheology had been optimized. Filtrate optimization was in fact not one of the main goals of this project.

The emulsion formed by Emulsifier 2137/3 is already strong and tight enough to give relatively low filtrate values (7-8 ml for the base muds) even at this high temperature without any filtrate reducer. Anyway, both commercially available fluid loss reducers and newly developed products have been tested. Fluid loss reducers commonly used in invert emulsion fluids are based on gilsonite (a naturally occurring weathered asphalt), amine-treated/causticized lignite, pliolite or polybasic acids. Among this range, polybasic acids have shown to be not stable at 340°F; the filtrate can therefore be controlled with the other types of chemicals.

New products have been synthesized, based on crosslinked polyacrylate esters in emulsion form, with different degrees of crosslinking. One of these products, called BF 2745 (Table 15), has shown to be extremely effective in controlling the filtrate even at very low dosages (Table 16 and 17). The thickness of the mud cakes were few mm and always proportional to the filtrate volume.

Organophilic clay

An organically modified clay (HT organoclay) has been used for all the tests as viscosifier / suspending agent (Table 18). HT organoclay is a highly purified smectite clay (hectorite), reacted with quaternary ammonium compounds to become oil soluble. This HT organoclay is normally used in HPHT wells because of its good thermal stability. Water is needed to act as activator to ensure full development of the rheological properties in the fully formulated mud.

A HT organoclay particle consists of a clay platelet having a long-chain organic compound (quaternary ammonium salt) bonded to its two faces. In the system containing the fully dispersed and activated organoclay additive, a gel structure is developed by edge-to-edge hydrogen bonding between hydroxyl groups on the organoclay platelet edges. The hydroxyl groups on adjacent organoclay platelets edges are bridged by water molecules, forming a three-dimensional gel structure. If the water bridge is not present, no gel structure is developed. Solvation of the long chain organic molecule tails makes them stand away from the clay platelet faces. To obtain full rheological effectiveness, the hydrogen bonding sites on the HT organoclay platelet edges should not be obstructed. The concentration of HT organoclay required in the system

has always been very low. Because of the high density and low oil / brine ratio, most of the viscosity is contributed by the solids and by the water droplets dispersed in the continuous oil phase. It has been demonstrated that changing the oil / brine ratio from 60/40 to 80/20, the HT organoclay concentration needs to be increased from 1 pound per barrel (1 ppb / 2.9 kg/m³) to 8 ppb (22.9 kg/m³) to obtain the correct rheological parameters and avoid ilmenite settling.

Comparison of fluid rheology with traditional field muds.

Figure 2 shows the rheological profile of muds used during drilling on Kristin compared to muds developed in this project. Well 6406/2-5 was a vertical well where the mud apparently behaved satisfactorily without any mud-related problems. The same mud was used in well 6406/2-5AT2 where the inclination was 35°. Excessive barite sag was observed and the rheology was therefore boosted to compensate. The result was mud with very high viscosity readings at high shear rates as shown in the figure. This mud had very high ECD and high surge and swab pressures, with problems during drilling and cementing of the liner.

The desired rheology profile of muds for drilling ERD wells is flat, with high readings at low shear rates (typically 10-12 at 3 rpm) to hinder sagging of weighting material and low viscosity at high shear rates to give minimum ECD. As demonstrated in the figure, a dramatic improvement of the rheology is obtained for the new mud systems developed in this project. By using advanced software for calculating ECD during drilling, the effect of shifting to this new mud system is shown to be a reduction in ECD increment of 50-60% compared to the mud used in well 6406/2-5AT2. This improvement can make it possible to drill ERD wells at Kristin with ECDs lower than the fracture pressure.

Possible Applications and Future Developments

During drilling, formation damage may occur by plugging of pore spaces with drilling fluid additives. Treatment with HCl acid is commonly used to remove the plugging minerals but, because of barite's virtual insolubility, formation permeability can not be easily restored. Ilmenite on the other hand is reactive with HCl and therefore would allow formation permeability to be restored; in addition size distribution of ilmenite should be ideal for minimizing formation plugging and damage.

For special applications, the weighting material can be totally eliminated from the fluid. Solids free heavy emulsions are very interesting drill-in fluids, since they will cause no formation damage due to the weighting material, such as it is often seen from barite. Furthermore, all formate brines are based on monovalent cations (Sodium, Potassium, Cesium) which eliminate the risk of damage due to scale formation.

Even though this mud system has been designed specifically for HTHP drilling, the fluid system based on heavy emulsions can have other applications. By using cesium formate and an

oil / brine ratio of 50/50, mud weight of 1.52 S.G. can be obtained without addition of weighting material. This can be a very interesting fluid since suspension of weighting material will no longer be required. The viscosity can be lowered, giving a mud which could be very interesting for drilling in areas with very narrow ECD limits, for slim hole drilling and for coiled tubing drilling.

The advantages of solids-free heavy emulsions are significant. The plastic viscosity of muds is greatly affected by the quantity of suspended solids. Solids free emulsions systems will exhibit lower plastic viscosities than conventional mud systems. This will result in lower equivalent circulating densities (ECDs) and lower parasitic pressure losses down-hole, resulting in greater drilling efficiency. These two effects are particularly important in slim hole drilling and coiled tubing where, because of the reduced pipe and annulus diameters, minimizing down-hole pressure losses (and hence ECDs) is essential to ensure good rates of penetration, while preventing the fracturing of the formation. Some test results of solids free emulsions are reported in Table 19. Only Emulsifier 2137/3 is used at a concentration of 18 g in 400 ml emulsion (45 kg/m³). Rheology is very stable before and after hot rolling and is not dependent on the S.G. but only on the oil / brine ratio.

Conclusions

A low solids oil based mud system has been developed by the use of heavy brines in the internal phase and by using a high brine content to give a heavy emulsion as a base for the mud system.

The systems have been tested and proven stable at temperatures as high as 170 °C.

By using cesium formate in the internal phase and ilmenite as weighting agent, 2.04 SG HTHP mud with solid content as low as 21% v/v was developed. This mud has very low rheology with a PV below 25 cP and gives a tremendous reduction in ECD during drilling compared to conventional oil based muds used up to date.

Solid free oil based mud of densities as high as 1.52 SG and with extremely low rheology can also be made using the same chemical package as developed for the HTHP mud. This solid free system can be very interesting for drilling of wells with very narrow ECD limits, for slim hole drilling and for coiled tubing drilling.

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Nomenclature

YP	Yield Point [lb/100ft ²]
PV	Plastic Viscosity [cP]
AV	Apparent Viscosity [cP]
BHR	Before Hot Rolling
AHR	After Hot Rolling

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Table 1 - Tests with Potassium Formate

Formulation (base mud) :

Synthetic Paraffin B
Emulsifier 2137/3
Wetting agent WA 11
HT Organoclay
Brine HCOOK 75% d = 1.56
ILMENITE

9
112
18
4
1
141.7
435

Oil / Brine ratio 60/40
S.G. 2.04
Ilmenite vol. % 27.5

Measurements at 120 F BHR

Added component	600	300	200	100	6	3	G ₀	G ₁₀	AV	PV	YP	ES
-	80	48	37	24	7	6	6	6	40	32	16	274
3 ppb lime	90	53	39	26	8	7	7	7	45	37	14	350
1 ppb BF 2745	101	61	47	31	10	8	8	8.5	50.5	40	21	250
20 ppb OCMA clay	118	69	53	34	10	8.5	9	9	59	49	20	250
35 ml seawater	100	58	44	29	8.5	7	7	8	50	42	16	230
35 ml cement slurry**	114	65	48	30	8	7	7	7	57	49	16	250

Measurements at 120 F AHR 16h at 340 F (170°C)

Added component	600	300	200	100	6	3	G ₀	G ₁₀	AV	PV	YP	ES	HPHT ml
-	98	62	49	33	11	9.5	10	10	49	36	26	210	11.6 (0.6+2.4)*
3 ppb lime	93	56	44	30	10	9	9	9	46.5	37	19	330	7.2 (0.8)*
1 ppb BF 2745	102	68	53	35	12	10	10	11	51	34	34	220	6.8 (0.4+0.6)*
20 ppb OCMA clay	135	90	71	48	15	13	13	13	67.5	45	45	225	18.4 (0.8+5.2)*
35 ml seawater	123	76	60	41	13.5	11	11	11	61.5	47	19	235	17.6 (1.2+4.8)*
35 ml cement slurry**	125	77	58	39	12	10.5	11	11	62.5	48	29	265	10 (0.8+1.2)*

* HPHT filtration at 340 F (170°C) , 500 psi; the first number in brackets is ml of emulsion and the second is ml of water

** cement slurry has been formulated with 66% cement Class G-HSR and 44% liquids v/v with fresh water, dispersant, fluid loss reducer and aged at 60-80 °C for 1 h.

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Table 2 – Test with Potassium Formate

Formulation :

	g	g
Synthetic Paraffin B	103.5	142.8
Emulsifier 2137/3	18	18
Wetting agent WA 11	4	4
HT Organoclay	1	8
Lime	3	0
Brine HCOOK 75% d = 1.56	133.6	69.1
ILMENITE	506.7	479

Oil / Brine ratio	60/40	80/20
S.G.	2.2	2.04
Ilmenite vol. %	32.2	30.4

Measurements at 120 F BHR

	HT Organoclay	600	300	200	100	6	3	G ₀	G ₁₀	AV	PV	YP	ES
S.G. 2.2; 60/40	1 ppb	115	67	50	33	9	8	8	8	57.5	48	19	370
S.G. 2.04; 80/20	4 ppb	61	35	26	17	6	5	5	6	30.5	26	9	255
S.G. 2.04; 80/20	8 ppb	79	48	37	25	9	8	8	10	39.5	31	17	280

Measurements at 120 F AHR 16h at 340 F (170°C)

	HT Organoclay	600	300	200	100	6	3	G ₀	G ₁₀	AV	PV	YP	ES
S.G. 2.2; 60/40	1 ppb	127	78	60	40	13	11	11	11	63.5	49	29	310
S.G. 2.04; 80/20	4 ppb	55	30	23	14	5	45	5	6	27.5	25	5	300
S.G. 2.04; 80/20	8 ppb	88	54	41	26	8	7	7	9	44	34	20	240

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Table 3 – Test with Cesium Formate

Formulation :

	g
Synthetic Paraffin B	122.2
Emulsifier 2137/3	18
Wetting agent WA 11	4
HT Organoclay	1
Brine HCOOCs d =2.23	229
ILMENITE	339.7

Oil / Brine ratio	60/40
S.G.	2.04
Ilmenite vol. %	21.6

Measurements at 120 F BHR

Added component	600	300	200	100	6	3	G ₀	G ₁₀	AV	PV	YP	ES
-	60	35	27	18	6	5	5	5	30	25	10	270
3 ppb lime	59	34	25	16	5.5	4.5	4.5	5	29.5	25	9	370
1 ppb BF 2745	71	43	32	21	7	6	6	6.5	35.5	28	15	290
20 ppb OCMA clay	80	49	37	25	8	7	7	7	40	31	22	340
35 ml cement slurry**	75	42	30	19	5	4	4	5	37.5	33	9	200

Measurements at 120 F AHR 16h at 340 F (170°C)

Added component	600	300	200	100	6	3	G ₀	G ₁₀	AV	PV	YP	ES	HPHT ml
-	86	54	43	29	9	8	8	8	43	32	22	185	13.6 (0.4+3.6)*
3 ppb lime	62	38	29	20	7	6	6	7	31	24	14	350	8 (0.5+0.5)
1 ppb BF2745	74	47	36	25	8.5	7	7	7.5	37	27	20	270	8 (0.2+0.6)*
20 ppb OCMA clay	96	57	41	21	8	6.5	6.5	7.5	48	39	18	180	18.6 (1+2.8)*
35 ml cement slurry**	85	50	38	25	8.5	7	7	8	42.5	35	15	230	17.8 (1.4+4.4)*

* HPHT filtration at 340 F (170°C) , 500 psi; the first number in brackets is ml of emulsion and the second is ml of water

** cement slurry has been formulated with 66% cement Class G-HSR and 44% liquids v/v with fresh water, dispersant, fluid loss reducer and aged at 60-80 °C for 1 h.

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Table n. 4 – Tests with Cesium Formate

Formulation :

	g	g
Synthetic Paraffin B	113	116.5
Emulsifier 2137/3	18	18
Wetting agent WA 11	4	4
HT Organoclay	1	1
Lime	3	3
Brine HCOOCs d = 2.23	212	-
Brine 50/50 K/Cs Formate d = 1.90	-	182
ILMENITE	419	392.5

Oil / Brine ratio	60/40	60/40
S.G.	2.2	2.04
Ilmenite vol. %	26.6	24.8

Measurements at 120 F BHR

S.G.	600	300	200	100	6	3	G ₀	G ₁₀	AV	PV	YP	ES
2.20	73	42	31	20	6	5	5	6	36.5	31	11	330
2.04	74	44	33	21	6.5	5.5	6	6	37	30	14	360

Measurements at 120 F AHR 16h at 340 F (170°C)

S.G.	600	300	200	100	6	3	G ₀	G ₁₀	AV	PV	YP	ES
2.20	84	51	39	27	9	8	8	8	42	33	18	320
2.04	80	50	39	27	10	9	9.5	9.5	40	30	20	290

Table n. 5 – Comparison Between Two Different Mineral Oils

Oil/Brine 60/40; S.G.: 2.04; Measurements at 120 F BHR

Base oil	Weighting agent	Wett. agent	600	300	200	100	6	3	G ₀ /G ₁₀	AV	PV	YP	ES
Synt. Paraffin A	Ilmenite	WA02	96	52	37	21	4	3	3/5	48	44	8	275
Synt. Paraffin B	Ilmenite	WA02	74	40	28	16	3.5	3	3/4	37	34	6	270

Measurements at 120 F AHR 16h at 340 F (170°C).

Base oil	Weighting agent	Wett. agent	600	300	200	100	6	3	G ₀ /G ₁₀	AV	PV	YP	ES
Synt. Paraffin A	Ilmenite	WA02	118	62	44	26	6	4	5/6	59	56	6	340
Synt. Paraffin B	Ilmenite	WA02	84	46	33	19	5	4	5/5	42	38	8	264

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Table n. 6 – Typical Properties of Two Different Mineral Oils

Property	Synthetic Paraffin A	Synthetic Paraffin B	METHOD
Density @ 15°C	814 g/l	811 g/l	ASTM D 4052
Saybolt color	+ 30	+ 30	ASTM D 156
Boiling Range:			
- Initial point	255°C	231°C	ASTM D 86
- Dry Point	325°C	265°C	
Flash Point	118°C	101°C	ASTM D 93
Viscosity @40°C	3.5 mm ² /sec	2.28 mm ² /sec	ASTM D 445
Total Aromatic Content	0.003%	0.001%	UV
Aniline Point	91°C	80°C	ASTM D 611
Pour Point	- 27°C	- 51°C	ASTM D 97
Sulfur Content	0.5 ppm	0 ppm	ASTM D 3120
Auto ignition temperature	> 230°C	> 230°C	ASTM E 659
Vapor pressure	0 mbar @ 37.8°C	> 0.01 kPa @ 20°C	
CAS No.	64741-77-1	64742-46-7	
EINECS No.	265-078-2	265-148-2	
Biodegradability	76.5%	95%	OECD 306
Aquatic toxicity:			
- <i>Acartia Tonsa</i>	LC50> 42.900 mg/l	LC50: 65.155 mg/l	ISO/PARCOM GL
- <i>Skeletonema Costatum</i>	EC50>100.000 mg/l	EC50>100.000 mg/l	ISO/PARCOM

Table n. 7 – Typical Properties of Different Brines

Brine	Concentration	S.G.	MW	M (mol/l)	Aw
CaCl ₂	40 %	1.40	111	5.15	0.39
CaBr ₂	52%	1.72	199.9	4.47	ND
TKPP	ND	1.73	330.4	ND	ND
HCOOK	75%	1.56	84.1	14.09	0.31
HCOOCs	82%	2.23	177.9	10.51	0.28
50/50	78.5%	1.90	n.a.	n.a.	0.29
HCOOK/HCOOCs					

Table n. 8 – Typical Properties of Formate Brines

Property	HCOOK	HCOOCs H ₂ O
Biodegradation (OECD 301-D)	92%	83%
Theoretical Oxygen Demand	3.42 mgO ₂ /l	4.05 mgO ₂ /l
EC ₅₀ 48 h with <i>Acartia Tonsa</i>	300 mg/l	340 ml/l
LC ₅₀ 72 h with Brown Shrimp (<i>Crangon Cragon</i>)	1300 ml/l	91 ml/l
LC ₅₀ 96 h with Rainbow Trout	3500 ml/l	2100 ml/l
EC ₅₀ 72 h with <i>Skeletonema Costatum</i>	3400 ml/l	1000 ml/l
HOCNS Classification for the North Sea	E	E

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Table n. 9 – Typical Properties of Two Different Weighting Agents

Property	Barite	Ilmenite
Chemical formula	BaSO ₄	FeTiO ₃
Specific Gravity	4.2-4.5 (normally 4.2)	4.5-5.1 (normally 4.6)
Hardness (Mohs Scale)	2.5-3.5	5-6
Particle size	<3% >74 micron <30% <6 micron	<3% >45 micron <10% <1micron
Acid solubility	Insoluble	Soluble
Hardness (Mohs Scale)	2.5-3.5	5-6
Crystal structure	Orthorhombic	Hexagonal

Table n. 10 – Mud Rheology with Two Different Weighting Agents

Oil/CaBr₂ Brine 60/40; S.G. 2.04; Measurements at 120° F BHR

Emulsifier	Wetting agent	Weighting agent	600	300	200	100	6	3	G ₀	G ₁₀	AV	PV	YP	ES
2137/3	WA02	Ilmenite	96	52	37	21	4	3	3	5	48	44	8	275
2137/3	WA02	Barite	112	59	41	23	4	4	4	5	56	53	6	1000

Measurements at 120 F AHR 16h at 340 F (170°C).

Emulsifier	Wetting agent	Weighting agent	600	300	200	100	6	3	G ₀	G ₁₀	AV	PV	YP	ES	HPHT (ml)
2137/3	WA02	Ilmenite	118	62	44	26	6	4	5	6	59	56	6	340	8
2137/3	WA02	Barite	126	69	48	29	7	6	6	6	63	57	12	620	N.D.

Table n. 11 – Mud Rheology with Increasing Concentrations of Primary Emulsifier

Oil/K formate brine 60/40; S.G. 2.04; Measurements at 120 F BHR

2137/3 concentration	Wetting agent	600	300	200	100	6	3	G ₀	G ₁₀	AV	PV	YP	ES
14 ppb	WA11	76	43	32	20	5,5	4,5	5	6	38	33	10	260
18 ppb	WA11	80	48	37	24	7	6	6	6	40	32	16	274
22 ppb	WA11	80	48	37	25	8	7	7	8	40	32	16	282

Measurements at 120 F AHR 16h at 340 F (170°C)

2137/3 Concentration	Wetting agent	600	300	200	100	6	3	G ₀	G ₁₀	AV	PV	YP	ES	HPHT ml
14 ppb	WA11	124	81	64	45	14	12	10	11	62	43	38	155	15,8 (1+3)*
18 ppb	WA11	98	62	49	33	11	9,5	10	10	49	36	26	210	11,6 (0,6+2,4)*
22 ppb	WA11	92	58	46	31	10,5	9	9	9	46	34	24	244	10 (1)

* HPHT filtration at 340 F (170°C) , 500 psi; the first number in brackets is ml of emulsion and the second is ml of water

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Table n. 12 – Typical Properties of the Primary and Secondary Emulsifier

Property	Emulsifier 2137/3	WA 11
Chemical description	Modified fatty acids polyamide	Modified imidazoline
Appearance	Viscous dark liquid	Orange liquid
Acid Number	30-35 mg KOH/g	50-60 mg KOH/g
Amine Number	9.5 mg KOH/g	22 mg KOH/g
Brookfield Viscosity	1800 cP	15 cP
Pour Point	< -10°C	< -10°C
Flash Point	> 79°C	> 60°C
Water solubility	Insoluble	Soluble
HLB (estimate)	3-7	8-11

Table n. 13 – Influence of Alkali in Potassium Formate Mud

Measurements at 120 F BHR

Alkali source	600	300	200	100	6	3	G ₀	G ₁₀	AV	PV	YP	ES
-	80	48	37	24	7	6	6	6	40	32	16	274
3 g Lime	90	53	39	26	8	7	7	7	45	37	14	350
2.5 g KOH	81	47	35	23	7	6	6	6	40.5	34	13	350

Measurements at 120 F AHR 16h at 340 F (170°C)

Alkali source	600	300	200	100	6	3	G ₀	G ₁₀	AV	PV	YP	ES	HPHT ml
-	98	62	49	33	11	9.5	10	10	49	36	26	210	11.6 (0.6+2.4)*
3 g Lime	93	56	44	30	10	9	9	9	46.5	37	19	330	7.2 (0.8)*
2.5 g KOH	88	52	40	26	9	8	8	8	44	36	16	270	9 (0.4+1.6)*

* HPHT filtration at 340 F (170°C), 500 psi; the first number in brackets is ml of emulsion and the second is ml of water

Table n. 14 – Influence of Alkali in Cesium Formate Mud

Measurements at 120 F BHR

Alkali source	600	300	200	100	6	3	G ₀	G ₁₀	AV	PV	YP	ES
-	60	35	27	18	6	5	5	5	30	25	10	270
3 ppb Lime	59	34	25	16	5.5	4.5	4.5	5	29.5	25	9	370

Measurements at 120 F AHR 16h at 340 F (170°C)

Alkali source	600	300	200	100	6	3	G ₀	G ₁₀	AV	PV	YP	ES	HPHT ml
-	86	54	43	29	9	8	8	8	43	32	22	185	13.6 (0.4+3.6)*
3 g Lime	62	38	29	20	7	6	6	7	31	24	14	350	8.0 (0.5+0.5)*

* HPHT filtration at 340 F (170°C), 500 psi; the first number in brackets is ml of emulsion and the second is ml of water

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Table n. 15 – Typical Properties of the Fluid Loss Reducer

Property	BF 2745
Chemical description	Polyacrylate ester at high degree of crosslinking in emulsion form
Appearance	Milky emulsion
Brookfield Viscosity	150 cP
Pour Point	< 0°C
Flash Point	> 100°C
Water solubility	Soluble

Table n. 16 – Effect of the FL Reducer in the Mud

Typical Oil/K formate 60/40, ilmenite, S.G. = 2.04; Measurements at 120 F BHR

Fluid loss reducer	600	300	200	100	6	3	G ₀	G ₁₀	AV	PV	YP	ES
-	80	48	37	24	7	6	6	6	40	32	16	274
1g BF2745	101	61	47	31	10	8	8	8.5	50.5	40	21	250
4g BF2745	137	92	71	48	16	14	14	15	68.5	45	47	270

Measurements at 120 F AHR 16h at 340 F (170°C)

Fluid loss reducer	600	300	200	100	6	3	G ₀	G ₁₀	AV	PV	YP	ES	HPHT FL* (ml)
-	98	62	49	33	11	9.5	10	10	49	36	26	210	11.6 (0.6+2.4)
1g BF2745	102	68	53	35	12	10	10	11	51	34	34	220	6.8 (0.4+0.6)
4g BF2745	153	122	97	68	24	20	20	21	76.5	31	91	238	3.5 (tr.)

* HPHT filtration at 340 F (170°C) , 500 psi; the first number in brackets is ml of emulsion and the second is ml of water

Table n. 17 – Effect of the FL Reducer in the Mud

Typical Oil/Cs formate 60/40, ilmenite, S.G. = 2.04; Measurements at 120 F BHR

Fluid loss reducer	600	300	200	100	6	3	G ₀	G ₁₀	AV	PV	YP	ES
-	60	35	27	18	6	5	5	5	30	25	10	270
1 ppb BF 2745	71	43	32	21	7	6	6	6.5	35.5	28	15	290

Measurements at 120 F AHR 16h at 340 F (170°C)

Fluid loss reducer	600	300	200	100	6	3	G ₀	G ₁₀	AV	PV	YP	ES	HPHT FL* (ml)
-	86	54	43	29	9	8	8	8	43	32	22	185	13.6 (0.4+3.6)*
1 ppb BF 2745	74	47	36	25	8.5	7	7	7.5	37	27	20	270	8.0 (0.2+0.6)*

* HPHT filtration at 340 F (170°C) , 500 psi; the first number in brackets is ml of emulsion and the second is ml of water

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Table n. 18 – Typical Properties of HT Organoclay

Properties	HT Organoclay
Composition	Organically modified hectorite clay
Color	Cream white
Form	Finely divided powder
Specific Gravity	1.7
Moisture	3% Max.

Table n. 19 – Solid Free Emulsions

Measurements at 120 F BHR

Oil / Brine	Brine	S.G.	600	300	200	100	6	3	G ₀	G ₁₀	AV	PV	YP	ES
50/50	HCOOK	1.2	38	24	19	14	5.5	5	5	7	19	14	10	213
50/50	HCOOCs	1.53	37	24.5	19	14	5.5	5	5	5	18.5	12.5	12	316
40/60	HCOOK	1.26	84	52	41	29	10.5	9	9	9	42	32	20	232
40/60	HCOOCs	1.68	83	52	41	29	10	9	9	9	41.5	31	21	385

Measurements at 120 F AHR 16h at 340 F (170°C)

Oil / Brine	Brine	S.G.	600	300	200	100	6	3	G ₀	G ₁₀	AV	PV	YP	ES
50/50	HCOOK	1.2	38	24.5	19	14	6	5	5	6	19	13.5	11	107
50/50	HCOOCs	1.53	38	25	20	14	6	5	5	5	19	13	12	183
40/60	HCOOK	1.26	82	50	39	27	10.5	9	9	9	41	32	18	93
40/60	HCOOCs	1.68	80	51	40	28	10.5	9.5	9	9	40	29	22	182

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Figure n.1 – Size Distribution of Barite and Ilmenite

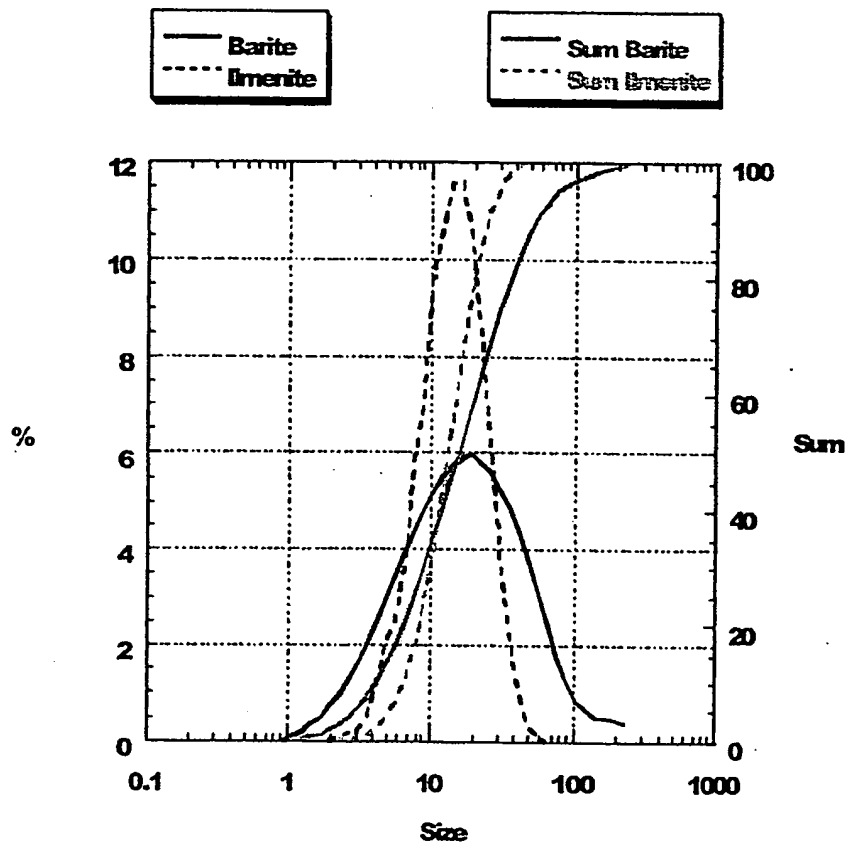
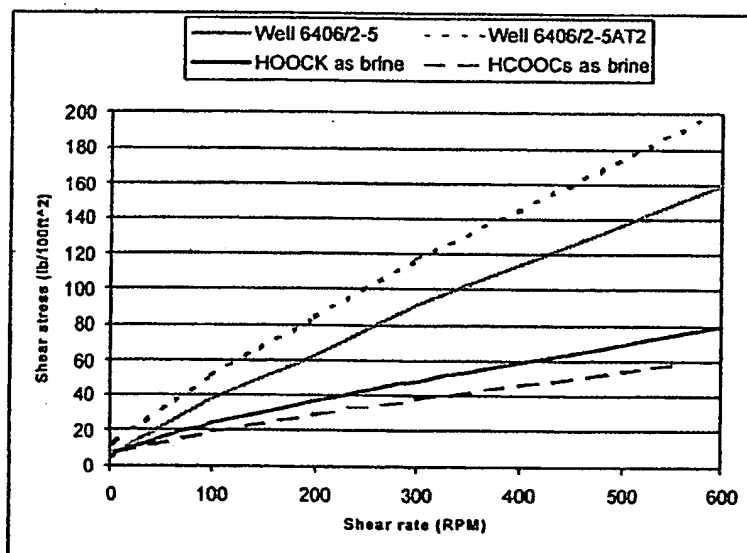
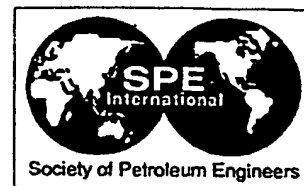


Figure n.2 - Rheological Profile of Kristin Field Mud and New Developed Mud System



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Development Process and Field Applications of a New Ester-based Mud System for ERD Wells on Australia's Northwest Shelf

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Abstract

Extended reach wells drilled from the Goodwyn Alpha platform are highly aggressive and have been drilled with a variety of invert-emulsion mud systems. Historically, mud system selection for these wells was based on compliance to environmental regulations and satisfaction of technical criteria. In order to take a more proactive approach to mud system selection and to raise environmental standards to new levels, an initiative was undertaken to replace the environmentally acceptable, and technically competent mud system being used on Goodwyn with a new ester-based system. Ester-based mud systems are considered the "system-of-choice" in terms of environmental acceptability and possess inherent lubricating qualities for torque and drag reduction.

This paper describes the development process and 4 successful field applications of the new ester-based mud system. A new ester, which exhibits the lowest kinematic viscosity of commercially available esters, was identified and selected for use. New and innovative technologies were introduced in the laboratory development and field applications to address barite sag, hole cleaning efficiency and hydrolytic stability.

The system development and field testing processes were enhanced by daily communication with the development teams in Aberdeen, Houston and Perth. Down-hole friction factors were significantly lower than modeled predictions. Barite sag problems encountered on previous wells were eliminated, and hole cleaning efficiency was optimized.

Introduction

The Goodwyn field is located off the Northwest Shelf of Western Australia. The field was discovered in 1971 by the Goodwyn-1 well, and is one of several large fault blocks located on the Rankin Trend, which form the northern margin of the Dampier sub-basin. The Goodwyn Field Development Plan was written in 1989 to encompass drilling 47 wells: 26 wells from Goodwyn A, 19 wells from a 2nd platform and 2 subsea wells. The plan was to drill the wells at maximum hole angles and horizontal departure of 55° and 4,000 meters, respectively. With the introduction of extended reach drilling, to 7,372 m horizontal step-out, the requirement for the second platform has possibly been eliminated.

The complexity of the Goodwyn extended reach drilling program increased as the wells progressed. The evolution of invert-emulsion fluids used on Goodwyn, from low toxicity oil-based muds (LTOBM) to ester-based muds (EBM), had a significant impact on the ability to expand the horizontal reach from the platform and the length of reservoir penetrated. At the conclusion of GWA Phases I & II, a total of 17 wells had been drilled to a maximum step-out of 7,372 m and horizontal section lengths of 2,300 m.

Drilling Fluids

Extended-reach drilling is a form of deviated drilling characterized by lengthy horizontal departures and aggressive hole angles. With consideration to eliminating drilling problems such as excessive torque and drag, poor hole cleaning, stuck pipe, low rates-of-penetration and well-bore stability, increasingly these wells are being drilled with invert-emulsion muds.^{1,2,3}

Invert-emulsion muds have evolved over the past several decades, primarily in response to government-imposed restrictions on the discharge of contaminated cuttings. LTOBM were introduced into the UK sector of the North Sea in the early 1980's and the number of wells drilled with LTOBM steadily increased in the late 1980's, with growing concern about the impact of discharges on aquatic life.

The industry began searching for alternatives that would provide the drilling performance of LTOBM, but without the

associated environmental liability, or HSE impact on rig personnel. Ester-based muds (EBM) were introduced in the early 1990's as a result of this initiative.^{4,5,6} EBM falls into a broad classification of invert-emulsion muds known as synthetic-based muds (SBM), and are classified according to their molecular structure.⁷ Early SBM were made from ester, acetal, ether or polyalphaolefin (PAO) base fluids, followed by internal olefins (IO), linear alpha olefins (LAO) or normal paraffins.

Several types of LTOBM, as well as paraffin and olefin-based SBM, were used in drilling the first 13 wells from the Goodwyn Alpha platform, and proved to be both technically competent and environmentally acceptable. A qualitative study was made of the environmental impact of a number of alternative muds/cuttings management options, including total containment, cuttings injection and the use of water or ester-based muds. Australian regulatory authorities, in line with North Sea equivalents, viewed EBM as a step change improvement on previous systems. In light of the regulatory authority's preference towards EBM, and Woodside's environmental policy, the decision was made to change from a high-performance olefin to an EBM. Additional considerations were:

- Improved economics of EBM (lower cost ester)
- Woodside found it difficult to justify the economics, risks and associated contingency planning for cuttings injection on Goodwyn, given the lack of cuttings injection experience in the area

The risks involved in replacing a technically competent, and environmentally acceptable mud system on these highly aggressive ERD wells were not trivial. It was felt that these risks could be mitigated by developing a new EBM tailored to the wells drilled on the Goodwyn platform.

Development Process

A project was undertaken to develop a new drilling fluid system suitable for drilling challenging ERD wells from the Goodwyn A platform. This system would be recognized as a new "standard" in terms of environmental acceptability on Australia's Northwest Shelf.

Team Communication. The development team was organized from the mud company's Technical Services and Engineering staff in Aberdeen and Houston, respectively. Joint responsibilities were shared by Operations in Perth and team leaders in Aberdeen and Houston. The time allotted to development was only 6 months and, thus required effective teamwork, communication and coordination of efforts across several time-zones to meet the dead-line. The development process was facilitated by frequent input and feedback/review from Woodside. By "inventing-on-schedule" this team developed a new and novel, environmentally safe EBM for use on the Goodwyn platform.

Ester Selection. The first step in the development phase was selection of an ester possessing technical qualities similar to

those of an olefin-based SBM, with the added environmental qualities. Several esters, based on vegetable and fish oil chemistry, were evaluated with consideration to:

- Environmental compliance
- Kinematic viscosity
- Elastomer compatibility
- Lubricity
- Alkaline and temperature stability

Environmental Compliance. Environmental compliance was the most important factor in the ester selection process. In the UK, the toxicity and biodegradability results of the new EBM were sufficient to gain a Category E rating (Table 1), which is the best environmental rating possible with allowance to discharge cuttings.

Kinematic Viscosity. The physical properties of three commercially available esters are shown in Table 2. Kinematic viscosity is an important physical property of base fluids because of its effect on the rheological properties and hydraulics. Fluids with a high kinematic viscosity generally exhibit high plastic viscosity, annular pressure losses and equivalent circulating densities (ECD's).

Kinematic viscosity also has an effect on the volume of ester needed to prepare an EBM system. Brine droplets emulsified into the ester increase plastic viscosity and a balance between volumes of ester and brine must be established. By using an ester with a low kinematic viscosity, higher volumes of brine can be used in formulating a finished barrel of mud. The net effect of this is to reduce mud costs and the environmental impact (from discharges), by reducing the volume of ester in an EBM. From Table 2 one can see that Ester A has the lowest kinematic viscosity of these commercially available esters.

Elastomer Compatibility. Another important performance measure is the compatibility of the ester with oilfield elastomers. Incompatibility between the ester and elastomer can result in changes to the volume and hardness of the elastomer, and subsequent field failures. Table 3 shows the results of elastomer testing in accordance with ASTM D471 and DIN 53521 protocols. These standards describe the requirements for the exposure to fluids and procedures to determine volume changes.

The elastomers tested were less affected by exposure to the n-paraffin and internal olefin-based SBM than to EBM. The esters can be rated in order of reactivity with the elastomers in the following order: Ester B, Ester A and Ester C. Compatibility tests on Ester C were carried out at lower temperature (100 °C), yet it was still the least compatible with elastomers. EBM's formulated with the Ester C have been extensively used with Nitrile elastomers, which suggests that Esters A and C should be equally compatible. In any case, the chosen ester had a damaging effect on some elastomers. This aspect always requires careful testing and monitoring.

Lubricity. As noted by Aarrestad² et al., torque and drag forces are limiting factors in the horizontal displacement of ERD wells. The use of water-based muds in drilling ERD wells is severely restricted because of their generally poor performance in torque and drag reduction. The inherent lubricating qualities of EBM make them ideal for torque and drag reduction in highly aggressive ERD wells.³ A relative comparison of friction coefficients of a high-performance WBM and several SBM is shown in Table 4. The data shows a step-reduction in friction is realized when using conventional SBM in lieu of WBM, with a further reduction occurring with EBM.

Ester Hydrolysis. Esters are susceptible to hydrolysis under conditions of high alkalinity and/or temperature. A low rate of hydrolysis indicates that the ester is chemically stable, which can extend usage in high temperature wells. This is an important consideration when using EBM in wells with high bottom-hole temperatures.

Ester A is produced from the esterification of salmon oil and isopropyl alcohol. Tests were conducted over a range of lime concentrations and temperatures to measure the levels of isopropyl alcohol produced. The amount of isopropyl alcohol liberated was measured by gas chromatography. Alkaline hydrolysis of Ester A begins at concentrations of free lime of 0.5 lbm/bbl (Figure 1). The temperature-induced hydrolysis of Ester A begins at ~ 163 °C (Figure 2).

Distillation. Laboratory tests show that volumes of Ester A cannot be measured directly using a standard 50 ml retort. Distillation tests at different ester-water-ratios were conducted. Comparison of the theoretical and measured test results allowed a correction factor of 1.08 to be established.

Emulsifier Selection. After ester selection, the next phase of the development process centered around the evaluation of surfactant chemistry. Using a novel technique introduced by Quintero⁸ et al., emulsifier efficiency was studied by measuring the size and stability of emulsified droplets using light scattering techniques.

Brine-in-oil emulsions were prepared and evaluated using surfactants, and blends of surfactants, with various hydrophilic/lipophilic (HLB) index values. HLB is related to the size and strength of the hydrophilic (polar) and the lipophilic (non-polar) groups of the surfactant molecule.

The distribution of particle sizes was measured using a Malvern Mastersizer. Droplet size determinations were made initially and after heat aging 16 hours at 121 °C (250 °F). The analyses of results were based on the average droplet size (D[4,3]) and the particle size <90 % (D[0,9]).

Weighting materials were not used during the screening process because of particle size overlap with the brine droplets. All surfactants evaluated formed a stable emulsion of brine in Ester A and the emulsion. The criteria used to evaluate emulsifiers were:

1. Average droplet size of the unweighted emulsion < 10 microns, initially and after heat aging
2. Difference between initial and heat aged average droplet size \pm 4 microns
3. HPHT filtration control was used to differentiate from criteria "2" above

Figure 3 shows an example of a poor surfactant for use with Ester A. The shift (increase) in droplet size after heat aging indicates poor emulsion stability. The droplet size distribution of the emulsifier selected for use with Ester A is shown in Figure 4. With this emulsifier the droplet size does not appreciably change after heat aging. The average droplet size is < 5 microns, which is ideal since an average droplet size < 10 microns indicates that optimum emulsion stability.

Additional tests were performed on this emulsifier and appear in Figure 5. After heat aging at 149 °C (300 °F), fluids were left static for a 14-days to allow coalescence of droplets. Using this emulsifier, the average droplet size for the olefin-based SBM varied from 5 to 20 microns, while the EBM ranged from 4 to 8 microns. The emulsifier was previously used in an olefin-based SBM on GWA 13 with good success. These results demonstrate the stability of the EBM emulsion and its resistance to coalescence under static conditions.

Organophilic Clay. Several organophilic clay types and chemistries were evaluated using dynamic oscillatory and traditional oilfield rheological test methodology. From this testing, DFE-434, an ester-specific organophilic clay, was selected for use with Ester A.

Rheological Modifier. Dynamic oscillatory and conventional rheological testing methodologies were also used for screening rheological modifiers. The tests were designed to evaluate the degree to which each additive modified the structure formed by the organophilic clay network. These were balanced against the contribution to viscosity, particularly plastic viscosity, measured with each additive.

DFE-433 was found to be the most effective rheological modifier and also served a secondary function for HPHT filtration control. HPHT filtration rates measured when using DFE-433 were such that further work evaluating HPHT fluid loss additives was not warranted.

Dynamic Oscillatory Tests. Dynamic oscillatory tests provide information about the efficiency of structured fluids that are not apparent in traditional rheological tests.⁹ In these tests the strain response to a sinusoidally varying stress is separated into in-phase and out-of-phase components. Viscoelastic materials exhibit a two component response because some of the energy applied is stored elastically and some is lost. Viscoelastic components are quantified as the elastic or storage modulus (G') and the viscous or loss modulus (G''), and used as sensitive probes of gel structures. The term "storage modulus" is used to describe G' since elastic energy is stored, whereas "loss modulus" is used to describe

G" since viscous energy is lost. G' is related to the "liquid-like" characteristics of the material, e.g. the flow behavior of a drilling mud. G' is related to "solid-like" behavior, e.g. how well a drilling mud will suspend solids.

Viscoelastic behavior can be sub-divided into linear and non-linear responses. The most common way of quantifying linear viscoelasticity is through dynamic oscillatory tests. Linear viscoelastic properties are observed when shear stress and strain are proportional. Small deformations are applied to the sample and the viscous and elastic responses are measured. The gel strengths of drilling muds are best measured using small deformations, i.e., through linear viscoelastic tests. Non-linear viscoelasticity implies that shear stress and strain are disproportionate. Large deformations are applied to the sample in non-linear viscoelastic tests. These tests measure the flow behavior of drilling muds, i.e. shear viscosity and shear thinning behavior.

Figures 6 & 7 show the results of dynamic oscillatory tests on a formulation containing DFE-434 and DFE-433. The base mud exhibits the classic profile of a 3-dimensional, linked network, as evidenced by the elastic modulus (G') dominating over the entire frequency region (Figure 6). The gel structure of the base mud exhibits dynamic recovery with time, meaning that the gel recovers after a period of high shear and immediately exhibits elastic behavior (Figure 7).

Optimized EBM System. Several classes of organophilic clays, surfactants and rheological modifiers were evaluated, individually and in combination with one another, in the laboratory development of the new EBM system. Advanced and insightful techniques, such as droplet size measurements and dynamic oscillatory rheological testing were utilized to develop the optimized formulation.

After extensive optimization testing in the Aberdeen and Houston laboratories, two formulations were developed based on satisfaction of the technical specifications listed in Tables 5 & 6. Product concentration studies were carried out for individual, and combinations of products. The primary difference between the formulations was the ester-water-ratio (80/20 and 90/10). The 80/20 EWR formulation was recommended for field testing, with the 90/10 EWR held as a contingency. The 80/20 EWR formulation is simple in that it contains only three components: 1) emulsifier, 2) organophilic clay and 3) dual-function additive for rheological modification and HPHT filtration control.

The rheological and filtration properties of this formulation appear in the form of "wave-curves" in Figures 8 & 9. Wave curves are line-graphs of discontinuous data that would otherwise be presented using bar-charts. The use of "wave-curves" allows one to observe changes in the properties mud from contamination in a single, continuous graph. The profile of the graph was also deemed important and a "flat" rheological profile (stable to contamination) was targeted.

Performance Tests. The 80/20 EWR formulation was subjected to performance tests based upon expected downhole

conditions in the 8 1/2" hole intervals. The mud weight in this section is typically 12.5 lbm/gal and bottom hole temperatures are in excess 112 °C.

Temperature Stability. The effects of temperature on the rheological and filtration properties of this formulation are shown in Figure 10. Plastic viscosity, yield point and HPHT filtration controls values were stable at temperatures up to 150 °C (302 °F). HPHT filtration control increased at temperatures above 165 °C (329 °F).

Static Barite Sag. Static barite sag tests were performed in accordance with the test specifications detailed in Table 5. Tests were performed by placing standard 500 ml heat age cells, at atmospheric pressure, in a static-age oven for 16-hours at 149 °C. The volume of free oil and difference in density of the mud column were measured afterwards. The 80/20 EWR formulation passed both specifications.

An additional test was performed using a modified consistometer, which was pressurized to 10,000 psi. The free oil and static sag values increased in the high pressure test, but were still within the test specifications. Barite sag was monitored during field operations on Goodwyn and none was detected. These results appear in Table 7.

Dynamic Barite Sag. Dynamic barite sag rates were modeled at minimum flow rates and maximum hole angles expected in the 12 1/4" hole interval. Dynamic flow loop tests were performed at a constant annular velocity (AV), for 30 minutes at 65 °C. Static tests were performed for 16-hours at 93 °C. The test results for the optimized 80/20 EWR formulation were:

- Δ Mud Weight at 127 ft/min AV = 0.17 lbm/gal
- Δ Mud Weight at 83 ft/min AV = 0.25 lbm/gal
- Δ Mud Weight at static = 0.78 lbm/gal

Specifications did not exist for dynamic barite sag tests, however, these levels were consistent with results from muds known not to exhibit dynamic barite sag in the field.

Return Permeability. Testing was performed to identify the effects of the new EBM on reservoir production using a Berea sandstone core and Hassler cell permeameter. The results from Table 8 indicate that the wall-cake formed is easily removed from breakout pressures and that the EBM does not impair reservoir production.

HPHT Rheology. Routine rheological tests do not consider the influence of downhole temperatures and pressures on the rheological behavior of the EBM. This is particularly important in ERD wells where hydraulics performance is critical for hole cleaning, ECD, bit and BHA hydraulics.

The Fann® Model 70 viscometer was used to determine the effects of temperature and pressure on the rheological properties of an olefin and the new EBM systems. The

benefits of the optimization work done in the laboratory development of the EBM are apparent from this testing.

Figure 11 shows the effects of temperature (at constant pressure) on the plastic viscosity of an olefin-based and new EBM fluids. While the EBM generally exhibits higher levels of plastic viscosity across the temperature spectrum, they are not proportional to the differences in kinematic viscosity between the olefin and ester base fluids.

Similar comparative testing, showing the influence of increasing temperature on the 6 rpm reading appears in Figure 12. The new EBM exhibits significantly higher 6 rpm readings compared to the olefin-based fluid, which is desirable for aiding hole cleaning efficiency.

Field Applications

A final report detailing the development process and findings was presented to the Goodwyn drilling engineering staff in Perth for approval of a field test.¹⁰ At the conclusion of the presentation, the decision was made to test the new EBM on the Goodwyn Alpha platform. Between October 1998 and August 1999 four extended reach wells (Tables 9-12) were drilled from the Goodwyn A platform using the new ester-based mud system.¹¹

Following Phase I of the Goodwyn drilling program, the "drilling-in-the-box" concept was introduced.¹² This defined a quality wellbore as a section that has been drilled producing a clean smooth wellbore by reducing doglegs, ledges and tortuosity that ultimately reduce the friction factor to allow casing to be run trouble free. The concept was adopted to maximize rates-of-penetration (ROP) while maintaining proper hole cleaning. The ROP envelope was constantly being pushed, with ROP's of 60 m/hr obtained on GWA17 while still maintaining proper hole cleaning.

Milestones from these 4 ERD wells were:

- Successful field introduction of the new EBM
- Woodside's longest ever 13 3/8" casing string run to 3507m (11,506 ft) on GWA14
- Woodside's longest ever 9 5/8" casing string run to 6249m (20,502 ft) on GWA17

GWA 14. The first field trial for the new EBM was in the 12 1/4" hole interval of GWA14. The inevitable teething problems occurred upon initial preparation of the new EBM at the liquid mud plant in Dampier. Viscosity fluctuations were observed in the mud plant, although concentrations were identical to those recommended from laboratory tests. The fluctuations caused great concern because they were unexpected, and could not easily be duplicated in laboratory simulations. Development team members from Aberdeen and Houston worked to resolve the problem and openly communicated findings to the Goodwyn drilling engineering staff.

The new EBM was extremely stable during the 12 1/4" hole interval. HPHT filtration control was easily maintained with minor additions of emulsifier, although filter-cake quality

suffered from the increased levels of low gravity solids. Aggressive centrifuging was required to control the buildup of low gravity solids and maintain stable mud properties.

When running 9 5/8" casing, drag was monitored and plotted using modeling software. Observations from drag modeling and field results indicated that the downhole friction factors were extremely low, and followed a better trend than what was predicted. The actual drag seen (Figure 13) when running casing was lower than expected and almost linear with depth. The cased-hole friction factor (CHFF) was 0.25, with open-hole friction factors (OHFF) averaging 0.2 (Table 11). This was a very successful casing run from a drag reduction point of view.

Innovative technology was utilized to prevent dynamic barite sag at the rig-site using the modern field viscometer shown in Figure 14.^{13,14} This instrument is an improvement over conventional 6-speed viscometers because of several unique features: 1) measuring capabilities at ultra-low shear rates, 2) separation of drive and measuring systems and 3) utilization of a computer acquisition system to record, store and analyze data accuracy.

The "Prevention Window" was developed for use with this viscometer as a tool to predict dynamic barite sag potential. Additionally, the "Prevention Window" optimizes the rheological profile of the fluid and can be used to balance viscosity levels for needed for ECD management and dynamic barite sag prevention. Viscometer data was compared to the limits of the "Prevention Window" and interpreted as follows:

- Viscosity levels below the Lower Limit correspond to a high potential for dynamic barite sag.
- Viscosity levels above the Upper Limit also indicate a low potential for dynamic barite sag, but are excessive in terms of requirements for barite sag prevention.
- Viscosity levels within the limits of the "Prevention Window" are preferred, and indicate a low potential for dynamic barite sag.

Figure 15 shows results taken at a depth of 6144 meters in the 12 1/4" hole on GWA14. The low shear rate viscosity values taken at 49 °C (120 °F) plot at the Upper Limit, indicating a low potential for dynamic barite sag. Barite sag was not observed when running 9 5/8" casing.

The EBM performed well through the course of drilling and logging the 8 1/2" hole section. A large quantity of cement, some of which was "green" or reactive, was drilled and effected the mud system in several ways. First, it was observed that attached to the edges of the bit and stabilizer blades were small particles of a plasticine-type material. It is believed that the combined effects of high bottom-hole temperature and alkalinity arising from drilling reactive cement caused localized hydrolysis of the ester, and formation of these particles. The second effect of drilling reactive cement was to increase HPHT filtration rates. The effects of alkaline conditions could not be clearly delineated because the HPHT test temperature was simultaneously increased from 121 °C to 149 °C in the 8 1/2" hole interval. Treatments were

made to reduce fluid loss with limited success. A supplemental filtration control additive was then used with positive effects on HPHT filtration and filter-cake quality.

The rheological properties of the EBM in this section were stable, even when flowline temperatures rose above 85°C and required continuous additions of water to maintain the ester-water-ratio. There were no serious problems encountered while drilling the 8 1/2" interval and the 7" liner was run and cemented at 7,695 meters.

GWA 15. The 12 1/4" section was drilled without problems in 27 days at a deviation of 86°. This was the second of the Goodwyn wells drilled with the new EBM, and the experience gained on GWA14 identified product concentrations necessary for prevention of barite sag and maintaining efficient hole cleaning. Wellbore integrity was stable even after several weather-related incidents and power failures, during one of which it was not possible to move drill pipe or circulate the mud for 1.25 hours.

Difficulty was seen in measuring the concentration of low gravity solids (LGS) in the mud in the 12 1/4" hole. Error arose in calculating LGS using retort and mass balance methods due to a waxy deposit left in the retort cell. This was compounded by the production of fine, powdered cuttings being generated during periods of sliding. The cyclic degradation of drilled solids to a colloidal particle size effected the rheological properties and drilling hydraulics. Constant centrifugation and dilution were required during intervals of sliding in order to reduce solids levels.

After setting 9 5/8" casing, the EBM on surface was centrifuged to reduce density to 10.8 lbm/gal. The EBM performed well through the course of drilling, logging, and casing the 8 1/2" hole section. Properties were generally very stable and there were no incidences of barite sag and the hole-cleaning efficiency was satisfactory. Hole cleaning efficiency was monitored and graded (1-5 scale) from surface observations of cuttings returned, drag while tripping and torque and drag while drilling. HPHT filtrate was again adversely affected by the initial change to testing at elevated temperature and treatments were made to bring it to within specifications.

GWA16. The 13 3/8" casing was displaced to EBM after drilling the shoe with a 12 1/4" bottom-hole assembly and conducting a formation integrity test (12.9 lbm/gal). The mud generally performed well, with stable mud properties throughout the interval. At TD, the hole was left open 5 days while logging, yet casing was run to bottom with few problems. This was considered a positive reflection on the EBM and on the hole conditions obtained.

The 8 1/2" interval was not a horizontal section, and thus differs from previous sections drilled with the EBM. Water was incorporated into the EBM while running 9 5/8" casing, which affected the EWR and increased rheological properties. Tight hole was encountered in this interval and there was some evidence of sections being over-gauged. The 8 1/2" hole was

plugged and abandoned, resulting in mild cement and spacer contamination to the EBM.

GWA17. The 13 3/8" shoe-track was drilled with the EBM in an attempt to prevent contamination of the EBM with cement. The displacement to EBM on resumption of drilling went well, with a clear interface. The 12 1/4" section was drilled in 10 days with two full trips, one for an MWD failure and the other for a bit change. In addition to these, some precautionary rotary back-washing and wiper trips were performed with a view to keeping the hole as clean as possible for the ambitious 9 5/8" casing run. The entire open hole interval was rotary back-washed and back-reamed before logging. The casing run went extremely well, with no pumping required to work the string down to the desired setting depth of 6,249 meters, although some losses were seen while circulating before cementing.

The rheological properties of the reconditioned mud delivered from the liquid mud plant increased when subjected to downhole shear and temperature, a condition also experienced on GWA 16. These properties were reduced and were fairly stable throughout the interval (Figure 16).

Hole cleaning appeared to be adequate, although 6 rpm readings were generally low. Comparisons of the rheological profile to the "Prevention Window" indicated a low potential for dynamic barite sag, which was confirmed by field observations.

The new EBM exhibited stable rheological and filtration control properties while drilling these 4 ERD wells. Figure 17 shows a several-fold increase in cumulative low gravity solids content of the EBM from GWA14 to GWA17. Over this interval, the percentage of drill solids having a particle size < 2 microns increased from 6 % (GWA 14) to 18 % (GWA17). A comparison of Figures 17 & 18 shows the influence of low gravity solids on plastic viscosity, however the EBM appears resistant to solids contamination and suitable for reconditioning and recycling.

Conclusions

1. A new EBM was "invented-on-schedule" for field testing in the 12 1/4" interval of GWA 14. The development process was facilitated by effective communication and coordination of efforts between the global development teams.
2. New and novel technologies, such as linear viscoelastic rheological and droplet size surfactant measurements, were used to rationalize the development of this system.
3. The system is simple, with robust filtration and rheological control generally achieved with only 3 additives.
4. The new system was instrumental in successfully drilling the 12 1/4" and 8 1/2" hole sections of the Goodwyn Phase II program.
5. Barite sag, hole cleaning or wellbore instability problems were not encountered on the four wells drilled. Innovative field technology was used to monitor the potential for dynamic barite sag.

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6. A constant focus on minimizing low gravity solids was required for rheological stability. The inaccuracy inherent of retorting solids made it difficult to quantify the effectiveness of the solids control equipment.
7. The EBM has excellent lubricity characteristics. Open and cased hole friction factors were extremely low.
8. The EBM remained stable throughout the project and was used and reconditioned many times over the 4 wells drilled.

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10. BIO-GREEN Development & Optimization Report for Woodside Offshore Petroleum Ltd., Baker Hughes INTEQ Drilling Fluids, June 1998.
11. Goodwyn A, Phase II Close-out, Woodside Energy Ltd., December 1999.
12. "Drilling Quality Wellbores" (WEL Doc No. A6000RD242)
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14. Dye, W., Hemphill, T., Gusler, W., and Mullen, G., "Correlation of Ultra-Low Shear Rate Viscosity and Dynamic Barite Sag in Invert-emulsion Drilling Fluids", SPE 56636, presented at the 1999 SPE Annual Technical Conference, Houston, Texas, October 3-6, 1999.

SI Metric Conversions

ft x 3.048 *	E-01 = m
°F (°F-32)/1.8	= °C
lbf/100 ft² x 4.778 026	E-01 = Pa
lbm/gal x 1.198 264	E+02 = kg/m³

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Table 1
Environmental Testing – Ester A

Test	Test Protocol	Specification	Result
72 hr EC ₅₀ <i>Skeletonema costatum</i>	ISO/DIS10253	>1000 mg/L	>10,000 mg/L
48 hr LC ₅₀ <i>Arcatia tonsa</i>	ISO T147 5C5 WG2	>1000 mg/L	>1,000 mg/L
10 day LC ₅₀ <i>Corophium volutator</i>		>1,000 mg/Kg	39,737 mg/Kg
28 day Aerobic biodegradation	OECD306	>60%	85 %
60 day Anaerobic biodegradation	ISO CD11734	>60%	>60 %
log Pow	OECD117	N/A	4.99

Table 2
Properties of Esters

Property	Ester A	Ester B	Ester C
Source	Fish Oil	Vegetable Oil	Vegetable Oil
Density (lbm/gal) 20 °C	7.17	7.09	7.17
Kinematic Viscosity, (cSt @ 40 °C)	5.5	8.3	6.0
Flash Point (ASTM D 92, °C)	175	150	179
Cloud Point (°C)	2	< -15	-
Hydrolytic Thermal Stability Limit (°C)	> 175	> 150	-

Table 3
Elastomer Compatibility

Fluid	Elastomer	Temp/72h	Volume Change	ΔHardness	Reactivity
Ester A	D	125 °C	7.9	-6	2
Ester A	F	125 °C	3.8	-2	1
Ester B	D	125 °C	3.4	-1	1
Ester B	F	125 °C	-2	0	1
Ester C	D	100 °C	8.1	-6	2
Ester C	F	100 °C	1.9	-3	1
N-paraffin	D	125 °C	3.9	-4	1
N-paraffin	F	125 °C	0	0	1
Internal Olefin	D	68.3 °C	3.9	-6	1
Internal Olefin	F	150 °C	-0.7	0	1

Elastomer D is Nitrile (NBR) rubber

Elastomer F is Hydrogenated Nitrile (HNBR)

Table 4
Lubricity Tests

Mud System	Coefficient of Friction
PHPA/Glycol WBM	0.28
Mineral Oil	0.20
Internal Olefin	0.19
Ester B	0.16
Ester A	0.15

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Table 5
Drilling Fluid Specifications

Mud Property	Specification
Density (lbm/gal)	12.5
Oil/Water Ratio	80/20 to 90/10
Water Phase Salinity	180 - 200 g/L (23.5 - 25.5% CaCl ₂ Brine)
Plastic Viscosity (cP)	ALAP
Yield Point (lbf/100 ft ²)	<18
Plastic viscosity/yield point ratio	0.8 to 1.5
10 minute Gel (lb/100 ft ²)	<20
Fann 6 rpm reading	12 - 14
HPHT Fluid Loss, ml	<4 (143 °C)
Static Barite Sag, lbm/gal	Δ Mud Weight [(MW top) - (MW bottom)] = <1.46 (143 °C)
Free Oil	<25 ml (143 °C) on base mud

Table 6
Contamination Studies

Contaminant	Specification
Drill Solids	10 % (wt./vol.) or 35 lbm/bbl
Seawater	10 % (vol./vol.) or 35 ml
Barite	Weight up to 2.0 lbm/gal

Table 7
Static Barite Sag

Temperature, °C	Pressure, psi	Free Oil (ml) Specification	Free Oil (ml) Actual	Δ MW Specification	Δ MW Actual
149	14.5	< 25	0.0	<1.46 lbm/gal	0.17 lbm/gal
149	10,000	N/A	3.1	N/A	0.16

Table 8
Return Permeability Testing

Test substrate	Berea Sandstone core
Mud overbalance	500 psi for 2 ½ hours.
Breakout pressure	5.0 psi.
Test Temperature (°C)	65
Return Permeability, %:	100

Table 9
Goodwyn Phase II Wells

Well No	GWA14	GWA15	GWA16	GWA17
Well Type	Producer	Injector	Producer	Producer
TD, meters	7713	6884	6146	6263
Horizontal Displacement, meters	6548	5641	4918	5200
Max Inclination,	96.54°	94.12°	64.78°	70.54°

Table 10
12 ¼" Intervals

Well	GWA14	GWA15	GWA16	GWA17
Well Type	Horizontal	Horizontal	Conventional	Conventional
Inclination	67 - 84°	61 - 86°	61°	67 - 56°
TD, meters	6142	5284	5477	6263

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Table 11
9 5/8" Casing & Cementing

Well	GWA14	GWA15	GWA16	GWA17
CHFF	0.25	0.15	0.24	0.20
OHFF	0.1 - 0.3	0.2 - 0.4	0.1 - 0.3	0.1 - 0.4
Planned Time, days	4.7	3.78	4.4	3.86
Actual Time, days	4.7	3.24	3.1	3.19

Table 12
8 1/2" Intervals

Well	GWA14	GWA15	GWA16
Inclination	84 - 96°	86 - 94°	64 - 57°
TD, meters	7713	6884	6146

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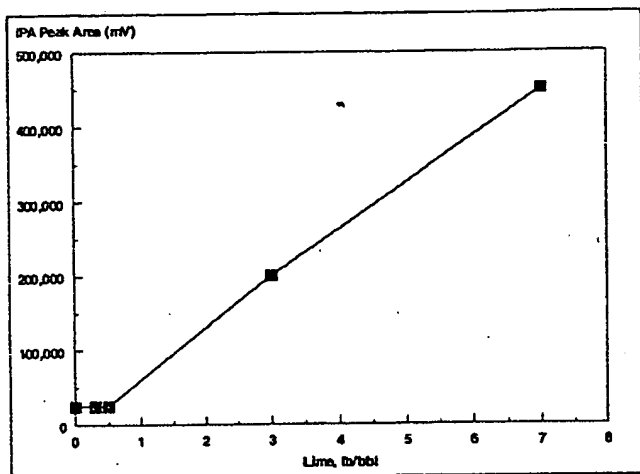


Figure 1 – Alkaline Hydrolysis

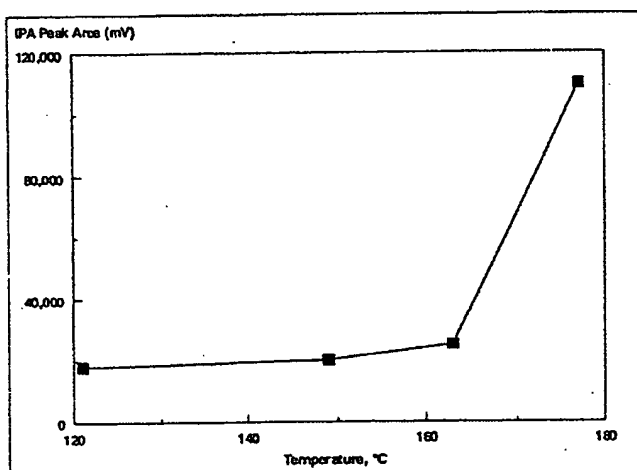


Figure 2 – Temperature Hydrolysis

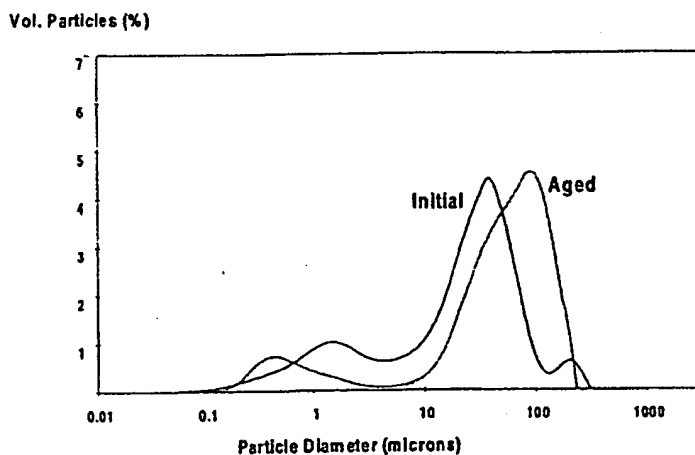


Figure 3 – Droplet Size Measurements – Poor Emulsifier

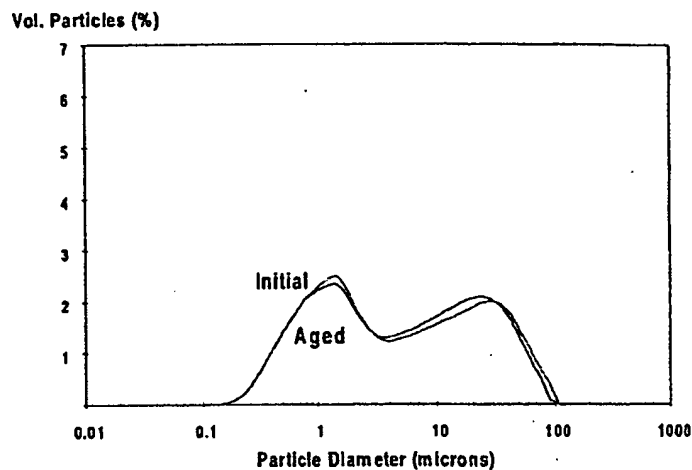


Figure 4 – Droplet Size Measurements – Preferred Emulsifier

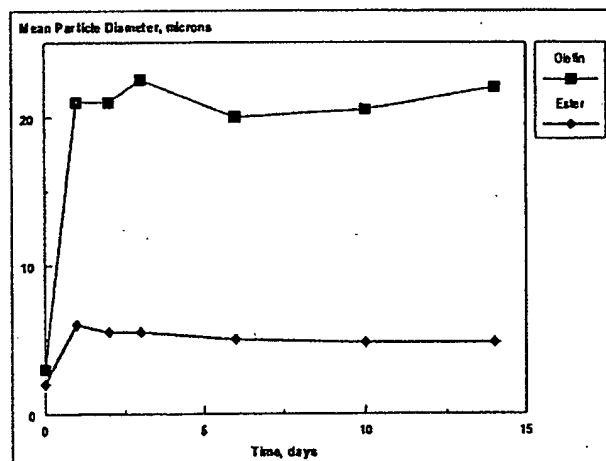


Figure 5 – Droplet Size Stability as Function of Time

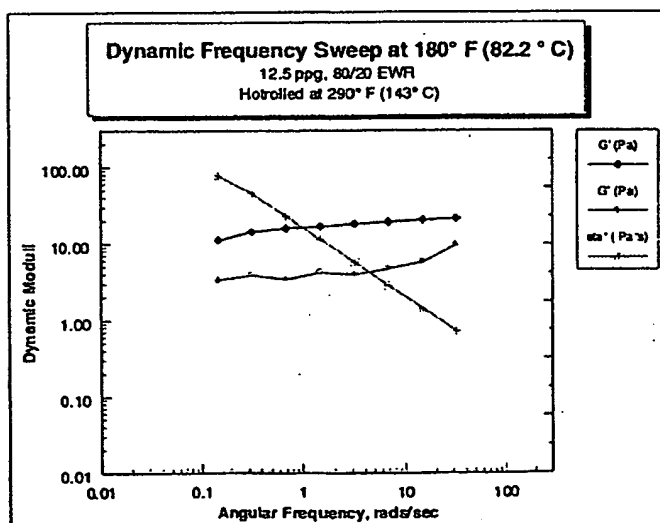


Figure 6 – Dynamic Frequency Sweep

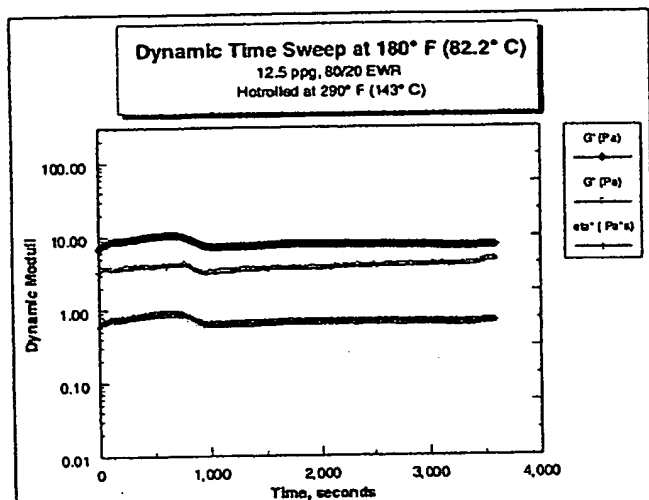


Figure 7 – Dynamic Time Sweep

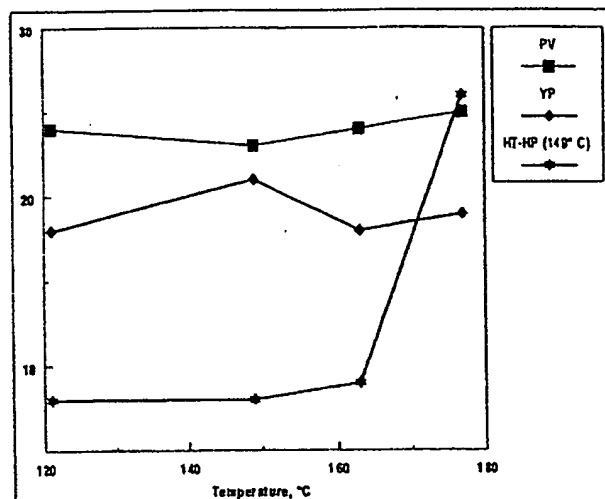


Figure 10 – Effects of Temperature on Properties-80/20 EWR

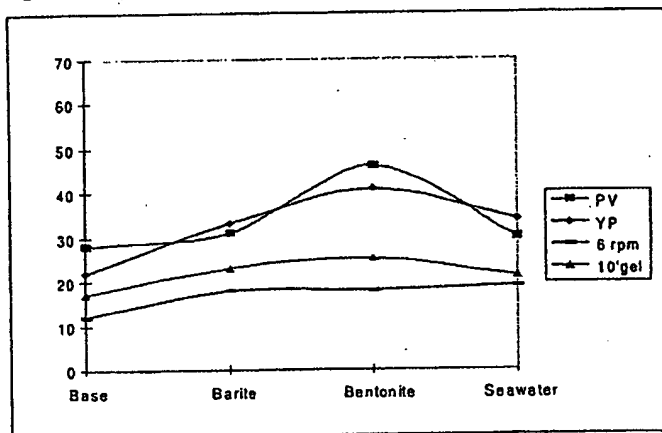


Figure 8 – Wave Curve – 80/20 EWR Formulation (Aged at 300° F)

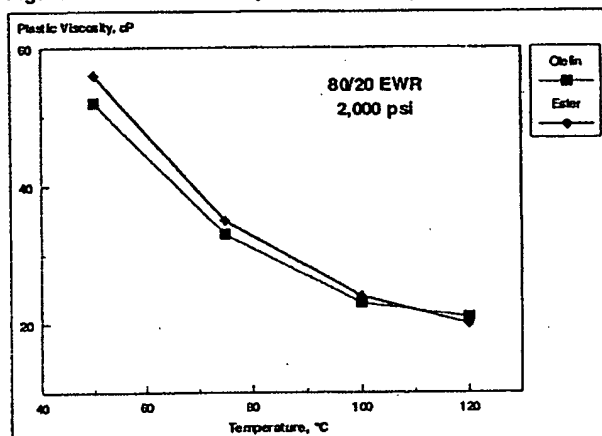


Figure 11 – HPHT Rheology – Plastic Viscosity Comparison

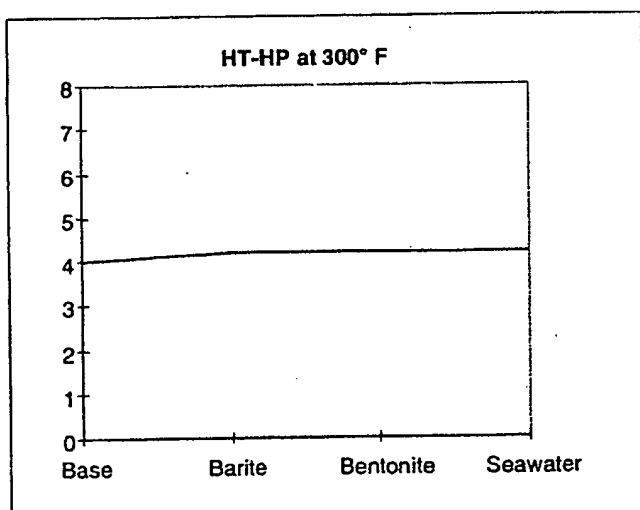


Figure 9 – Wave Curve – 80/20 EWR Formulation (Aged at 300° F)

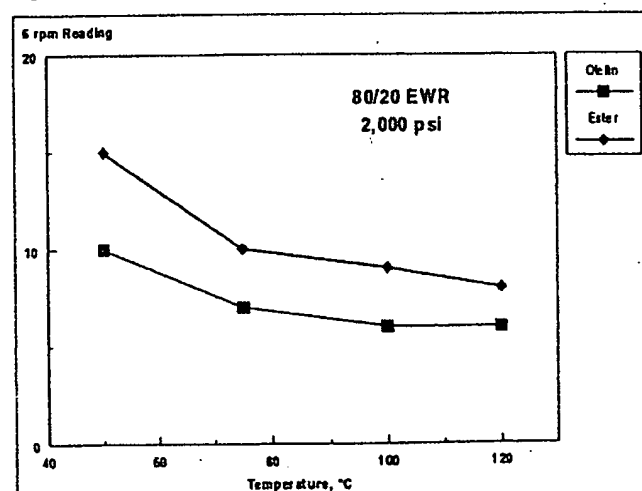
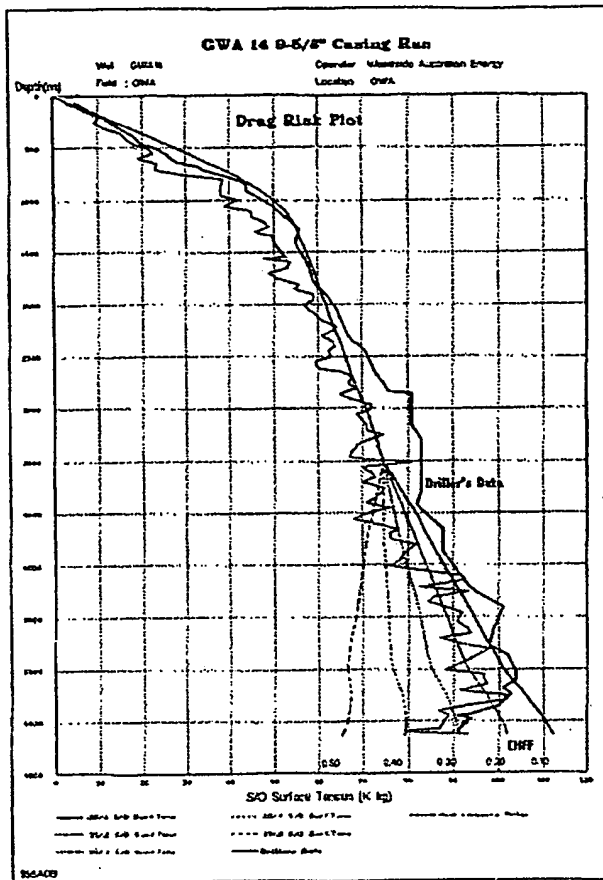


Figure 12 – HPHT Rheology – 6 rpm Reading Comparison

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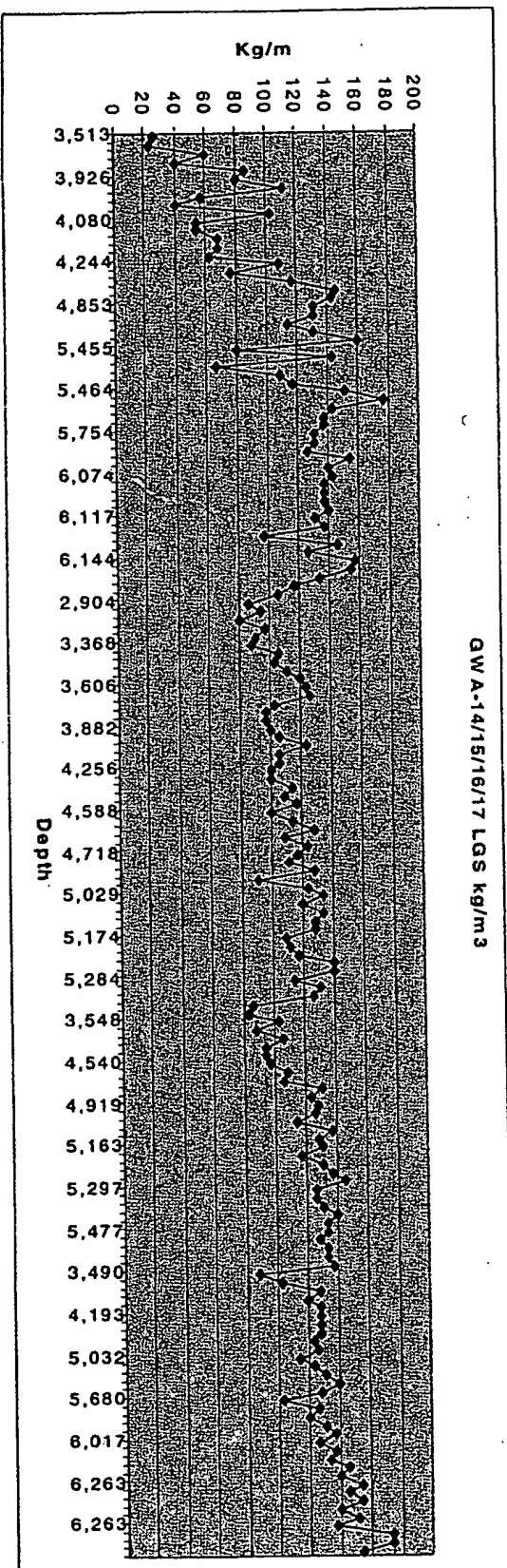


Figure 17—Cumulative Increase In Drill Solids- 12 1/4" Intervals

GW A-14/15/16/17 PV cP @ 66C

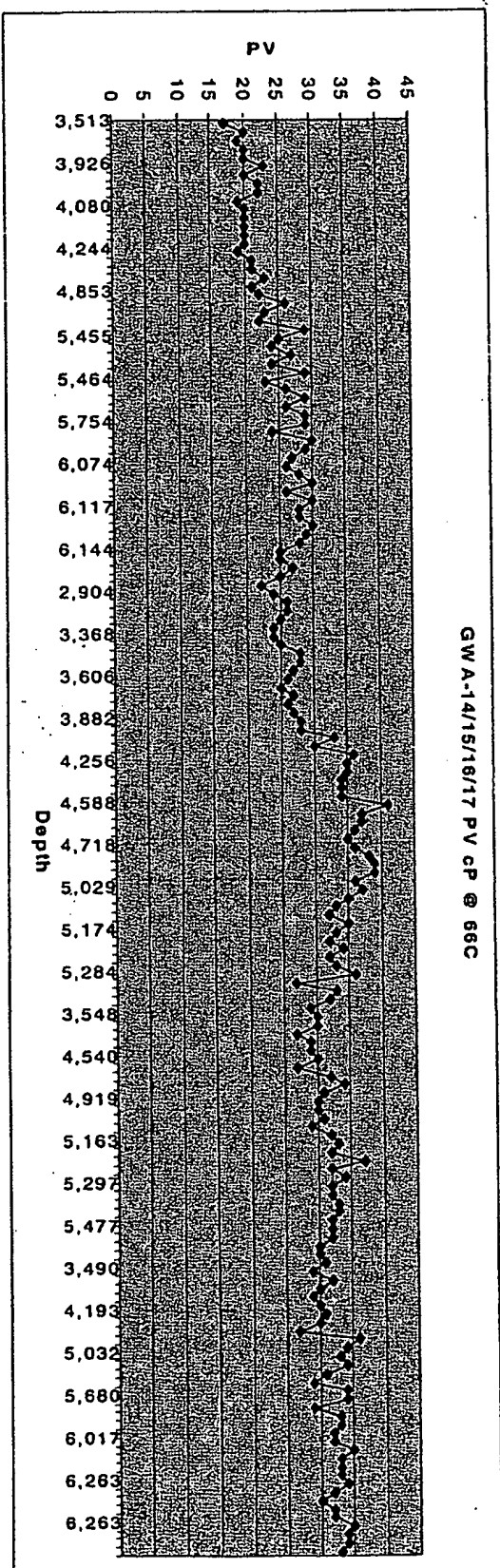


Figure 18—Cumulative Increase In Plastic Viscosity- 12 1/4" Intervals

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- (54) UTILISATION DE COMPOSES TENSIO-ACTIFS A BASE DE GLYCOSIDE ALKYLE DANS DES FLUIDES DE
FORAGE A BASE D'EAU ET D'HUILE ET AUTRES AGENTS DE TRAITEMENT POUR PUIITS DE FORAGE
(54) USE OF SURFACE-ACTIVE ALKYL GLYCOSIDE COMPOUNDS IN WATER- AND OIL-BASED DRILLING
FLUIDS AND OTHER DRILL-HOLE TREATMENT AGENTS

(57)

Described is the use of surface-active alkyl glycoside compounds as ecologically compatible emulsifiers of the W/O type and O/W type, respectively, in fluid and pumpable drilling fluids and other fluid drilling-hole treatment agents which comprise a continuous or a dispersed oil phase together with an aqueous phase and which are suitable for an environment-ally acceptable exploitation of geological resources, for example oil or natural gas deposits. The invention further relates to inverted drilling fluids which are suitable for a non-polluting exploitation of geological resources and contain a continuous oil phase and, present therein, a dispersed aqueous phase together with emulsifiers, further conventional auxiliary agents such as thickeners, fluid-loss additives, weighting agents, water-soluble salts and/or alkali reserves, said inverted drilling fluids being characterized in that they contain surface-active alkyl glycoside compounds of formula (I) as emulsifier or as an emulsifier component together with an ecologically compatible continuous oil phase.

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(54) Titre : UTILISATION DE COMPOSES TENSIO-ACTIFS A BASE DE GLYCOSIDE ALKYLE DANS DES FLUIDES DE FORAGE A BASE D'EAU ET D'HUILE ET AUTRES AGENTS DE TRAITEMENT POUR Puits DE FORAGE
(54) Title: USE OF SURFACE-ACTIVE ALKYL GLYCOSIDE COMPOUNDS IN WATER- AND OIL-BASED DRILLING FLUIDS AND OTHER DRILL-HOLE TREATMENT AGENTS

(57) Abrégé/Abstract

Described is the use of surface-active alkyl glycoside compounds as ecologically compatible emulsifiers of the W/O type and O/W type, respectively, in fluid and pumpable drilling fluids and other fluid drilling-hole treatment agents which comprise a continuous or a dispersed oil phase together with an aqueous phase and which are suitable for an environmentally acceptable exploitation of geological resources, for example oil or natural gas deposits. The invention further relates to inverted drilling fluids which are suitable for a non-polluting exploitation of geological resources and contain a continuous oil phase and, present therein, a dispersed aqueous phase together with emulsifiers, further conventional auxiliary agents such as thickeners, fluid-loss additives, weighting agents, water-soluble salts and/or alkali reserves, said inverted drilling fluids being characterized in that they contain surface-active alkyl glycoside compounds of formula (I) as emulsifier or as an emulsifier component together with an ecologically compatible continuous oil phase.

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Abstract of the Disclosure

Described is the use of surface-active alkyl glycoside compounds as ecologically compatible emulsifiers of the W/O type and O/W type, respectively, in fluid and pumpable drilling fluids and other fluid drilling-hole treatment agents which comprise a continuous or a dispersed oil phase together with an aqueous phase and which are suitable for an environmentally acceptable exploitation of geological resources, for example oil or natural gas deposits.

The invention further relates to inverted drilling fluids which are suitable for a non-polluting exploitation of geological resources and contain a continuous oil phase and, present therein, a dispersed aqueous phase together with emulsifiers, further conventional auxiliary agents such as thickeners, fluid-loss additives, weighting agents, water-soluble salts and/or alkali reserves, said inverted drilling fluids being characterized in that they contain surface-active alkyl glycoside compounds of formula (I) as emulsifier or as an emulsifier component together with an ecologically compatible continuous oil phase.

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Abstract of the Disclosure

Described is the use of surface-active alkyl glycoside compounds as ecologically compatible emulsifiers of the W/O type and O/W type, respectively, in fluid and pumpable drilling fluids and other fluid drilling-hole treatment agents which comprise a continuous or a dispersed oil phase together with an aqueous phase and which are suitable for an environmentally acceptable exploitation of geological resources, for example oil or natural gas deposits.

The invention further relates to inverted drilling fluids which are suitable for a non-polluting exploitation of geological resources and contain a continuous oil phase and, present therein, a dispersed aqueous phase together with emulsifiers, further conventional auxiliary agents such as thickeners, fluid-loss additives, weighting agents, water-soluble salts and/or alkali reserves, said inverted drilling fluids being characterized in that they contain surface-active alkyl glycoside compounds of formula (I) as emulsifier or as an emulsifier component together with an ecologically compatible continuous oil phase.

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USE OF SURFACE-ACTIVE ALKYL GLYCOSIDE COMPOUNDS
IN WATER- AND OIL-BASED DRILLING FLUIDS
AND OTHER DRILL-HOLE TREATMENT AGENTS

The invention relates to the use of selected emulsifiers having an increased ecological compatibility for the production of fluid dispersed systems which are present either as W/O inverted emulsions comprising a continuous oil phase or as aqueous emulsions containing a dispersed oil phase and which are suitable for the technical application within the field of use of fluid drill-hole treatment agents. Referring to a characteristic example for agents of this kind, the invention is described hereinbelow by way of oil-based and water-based drilling fluids, respectively, and drilling muds formed therewith. However, the field of application of the modification according to the invention of auxiliary liquids of the kind involved here is not limited thereto, while it also includes in particular the areas of spotting fluids, spacers, auxiliary liquids for workover and stimulation and for fracturing.

More particularly, the invention substantially influences the ecological compatibility of said auxiliary agents which are being worldwide used today by employing selected and, more specifically,

ecologically acceptable types of emulsifiers. In its preferred embodiment the invention intends to use said biologically acceptable emulsifiers simultaneously in combination with oil phases having an increased environmental compatibility and especially a biological degradability.

In the area of liquid sweeping systems for rock-drilling to bring-up the removed drill cuttings, the so-called inverted drilling muds are of excellent importance which, based on W/O emulsions, contain a dispersed aqueous phase in the continuous phase. The content of the dispersed aqueous phase usually is within the range of from about 5 to 50% by weight.

However, also known are water-based drilling fluids comprising an emulsified dispersed oil phase (O/W type), the oil content of which may range from some percent to about 50% by weight. O/W emulsion fluids of this kind exhibit a number of considerable advantages over merely water-based fluid systems.

The stabilization of each of the selected dispersion forms requires the use of appropriate emulsifiers either of the W/O type (inverted fluids) or of the O/W type (emulsion fluids), respectively. Hereto, reference is made to the pertinent literature, for example, G. R. Gray, H. C. H. Darley, "Composition and Properties of Oil Well Drilling Fluids", 4th Edition, Gulf Publishing Co., Houston, London 1981, especially pages 51, 64 and 320 et seq.

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Today the oil phases of drilling fluids of the type described here and comparably composed other drill-hole treatment agents in practice are almost exclusively formed by mineral oil fractions. This involves a considerable environmental pollution, if, for example, the drilling muds directly or via the drilled rock will infiltrate the environment. Mineral oils are only difficult to decompose and are virtually not anerobically degradable at all and, thus, to be rated as long-term pollutants. Nevertheless, even if these oil phases as the main constituent or at least a substantial portion of the drilling fluid make a significant starting point for ecological considerations, an equivalent attention will have to be paid also to the other components of such multi-component systems. Here, the emulsifiers are of specific importance. Compounds of this type, in accordance with the intended use thereof, are highly active substances already at a low concentration which are known to be capable of an intense interaction with the vegetable or animal organism.

Summary of the Invention

The present invention substantially improves the working agents of the described type based on continuous or dispersed oil phases in admixture with aqueous phases, in appreciation of the ecological compatability thereof, over the working agents of this kind as common to-day. More specifically, the invention, for the field of use as involved here, provides emulsifiers and/or emulsifier combinations which have been per se known and have been described to be environmentally compatible to a high degree, while they have not been put into use in the field of use involved here. In the preferred

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embodiment of the invention, these environmentally compatible emulsifiers of the W/O type or of the O/W type are to be employed in combination with oil/water phases, where the oil phases themselves have an increased ecological compatibility and, more specifically, are capable of being decomposed by natural degradation mechanisms doing little harm to the environment.

Other than in the operating examples, or where otherwise indicated, all numbers expressing quantities of ingredients or reaction conditions used herein are to be understood as modified in all instances by the term "about".

The invention provides the use of per se known surface-active alkyl glycoside compounds ecologically compatible or acceptable compounds which, depending on their constitution and kind of interaction with the surrounding system are to be classified as W/O emulsifiers or as O/W emulsifiers.

Thus, in a first embodiment, the invention relates to the use of surface-active alkyl glycoside compounds of the W/O type and/or O/W type, as ecologically compatible emulsifiers, in fluid and pumpable drilling fluids and other fluid drilling-hole treatment agents which comprise a continuous or a dispersed oil phase together with an aqueous phase and which are suitable for an environmentally acceptable exploitation of geological resources, for example oil or natural gas deposits.

Of particular importance in this context are the corresponding inverted drilling fluids which in a continuous oil phase contain a dispersed aqueous phase together with emulsifiers and further conventional auxiliary agents such as thickeners, fluid-loss

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additives, weighting agents, soluble salts and/or alkali reserve. In this embodiment according to the invention there is provided the use of surface-active alkyl glycoside compounds of the W/O type as emulsifier or at least as a component of an ecologically compatible emulsifier system.

Preferred is the use of emulsifiers based on surface-active alkyl glycoside compounds in combination with environmentally compatible ester oils, oleophilic alcohols and/or corresponding ethers as continuous or dispersed oil phase. Here particular reference is to be made to pertinent developments by applicant describing, in a greater number older patent applications, proposals for substituting the previously common mineral oil fractions with ecologically compatible readily degradable oil phases. Thereby, various types of substituting oils have been presented which may also be used as mixtures. They include selected oleophilic monocarboxylic acid esters, selected polycarboxylic acid esters, at least largely water-insoluble alcohols which are fluid under the operation conditions, corresponding ethers and selected carbonic acid esters. In summary, reference is made here to the older Canadian Patent Applications Nos. 2,006,010; 2,006,009; 2,047,697; 2,047,706; 2,009,689; 2,009,688; 2,051,624; 2,050,935; 2,084,780; and 2,085,610. All of the older

applications mentioned here relate to the field of oil-based drilling fluid systems, especially of the W/O inverted type. Water-based emulsion fluids using these oil phases of an increased degradability have been described in the older Canadian applications

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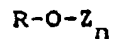
2,058,636; 2,057,005; 2,057,061; 2,084,780; and
2,085,610 as already mentioned.

The invention, in its most important embodiment, comprises the use, in combination, of the above-described emulsifiers of the class of the surface-active alkyl glycoside compounds together with dispersed or continuous oil phases of the type described last.

Detailed Description of the Invention

Surface-active alkyl glycoside compounds and the preparation thereof have been described in detail in the state of prior art, while emphasis so far has been laid on the use thereof as O/W emulsifiers - for example in the context of detergents and cleansers. In this context, reference is made to the DE-A1 38 33 780 and the primary literature quoted therein. A more recent proposal - cf. hereto the DE-A1 37 20 330 - provides the use, in combination, of alkyl glycosides within the scope of the so-called tertiary recovery of crude oil from appropriate deposits.

The alkyl glycoside compounds - as above - which are now to be used for the intended use according to the invention may be characterized by the following formula
(I)



(I)

wherein

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R in said formula represents linear and/or branched alkyl which may be saturated and/or olefinically unsaturated and has at least 7 carbon atoms in the moiety R. Preferred are corresponding moieties R having from 8 to 22 carbon atoms.

Z represents one or more moieties of aldoses and/or ketoses, among which here especially the hexose and/or pentose moieties are to be considered.

n characterizes the random oligomer distribution of the moieties Z. Numerically n represents a number of from 1 to 10 on the average, preferably of from 1.1 to about 5. Of particular importance are alkyl glycoside compounds having the general formula (I) wherein the numerical value of n is within the range of from about 1.2 to 2.5.

The term surface active alkyl glycoside compounds as used according to the invention is meant also to include the corresponding reaction products of sugars and monofunctional alcohols. As the sugar components in the widest sense there are to be contemplated the aldoses and ketoses designated as glycoses. There may be mentioned glucose, fructose, mannose, galactose, talose, gulose, allose, altrose, idose, arabinose, xylose, lyxose and ribose. For the preparation of the alkyl glycoside compounds aldoses are preferred to be used because of their higher reactivity. Among the aldose special importance is attributed to glucose due to its easy accessability and availability in commercial amounts.

The monofunctional alcohols employed for the acetalization, more particularly, are the surfactant

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alcohols having from 8 to 22 carbon atoms as commercially available on a large scale, among which native and/or synthetic alcohols are usable. Native alcohols are known to be obtained from the hydrogenation of fatty acids and fatty acid derivatives. Typical synthetic components are the known oxoalcohols and/or Ziegler alcohols. The alcohols themselves may be saturated, but they may be olefinically unsaturated as well. Straight-chain alcohols are of particular importance because they are quickly and trouble-free degradable. However, also branched alcohols, for example those of the kind of the oxoalcohols, are to be considered as ecologically compatible components and are suitable for acetalizing to form the alkyl glycoside compounds of the type used in the invention.

Alkyl glycoside compounds are excellent emulsifier components within the scope of the invention not only because of their biologic acceptability, but they are known to exhibit considerable alkali stability in the form of acetals. Drilling-hole treatment agents of the kind involved here, and especially drilling fluids, as a rule are composed such as to include alkali reserves, for example in order to be capable of counteracting the invasion of acidic reactants from the drilled rock. Said alkali stability of the alkyl glycoside compounds is an essential feature of the suitability thereof in practical use. At the same time they provide - depending on their specific structures - highly stable W/O emulsions.

The classification of the emulsifiers in each of the classes mentioned above is in a per se known manner governed by the ratio of the oleophilic portions

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in a given molecule to the hydrophilic portions of said molecule. The assignment may be achieved by way of the so-called HLB value; thereby the typical W/O emulsifiers are known to be characterized by comparably low HLB values - such as those within the range of from 3 to 11 or 12 - whereas the classical O/W emulsifier will occupy the higher range of the numerical HLB values. Also in the field as here concerned of the drilling hole treatment agents the above classification is made use of; cf. hereto, e.g., the literature reference Gray, Darley loc. cit., page 321, as quoted above.

The preferred functionability of each of selected alkyl glycoside compounds having the general formula (I) is derived from its structural members. The oleophilic molecule portion is coined by the moiety R of said formula. The sugar moiety Z, and here especially the oligomer distribution thereof - represented by the random numerical value for n - will form the hydrophilic molecule portion. Accordingly, W/O emulsifiers of this kind are characterized by having markedly oleophilic molecule portions with a restriction of the hydrophilic molecule portion, while the reversed situation is applicable to the case of the typical O/W emulsifiers.

Accordingly, for the stabilizing of W/O emulsions there are particularly suitable those compounds of the general formula (I) which at least partially, and preferably to a prevailing extent, comprise moieties R having 10 and more carbon atoms, and preferably at least 12 carbon atoms. Alcohol moieties of this kind comprising 16 to 18 carbon atoms may be of particular importance for technical as well as economical reasons. At the same time here the random mean value n for the

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glucose moiety as usually present is restricted to values below about 2.5 and preferably to maximum values of about 2. In preferred embodiments n may be within the range of from about 1.2 to 1.8.

Typical O/W emulsifiers, on the other hand, are the alkyl glycoside compounds as described in the quoted DE-A1 38 33 780 for washing and cleaning agents, which alkyl glycoside compounds are derived, for example, from C₁₀₋₁₄-alcohols. Here the numerical value of n may reach higher values within the range as indicated. However, it has been known that among the alkyl glycosides based on these comparably lower alcohols having about 8 to 14 carbon atoms highly active O/W emulsifiers are obtained also in the case that numerical value of n is, for example, within the range of from about 1.2 to 1.5. It is one characteristic feature with respect to the use of the alkyl glycoside compounds within the teaching of the invention that relatively easy shifts in the molecular structure may influence the suitability of the respective component(s) while, however, it is likewise a characteristic feature that among the compounds which are interesting under a preparation-technological aspect there is a relative large group of compounds suitable as stabilizing emulsifiers of the W/O type as well as of the O/W type. Here the type of emulsion formed is to a high degree co-determined by the total composition of the particularly involved drilling fluid or the corresponding drilling mud.

The alkyl glycoside-based emulsifiers, in a preferred embodiment, are employed as the essential components forming the type of emulsion and stabilizing the emulsion. Nevertheless the teaching according to the

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invention also includes mixed systems in which alkyl glycosides are used together with other emulsifier components. It is preferred that these other emulsifier components on their own are ecologically compatible; in this context reference may be made to applicant's older Canadian Patent Application No. 2,075,208

wherein selected ether-based and di-salt-based emulsifiers, respectively, for oil-based inverted emulsions have been described.

If such emulsifier mixtures are used, then in preferred embodiments of the invention the alkyl glycoside compounds constitute at least 10% by weight, and preferably at least 50% by weight, of the respective emulsifier system.

The alkyl glycoside compounds may be used in amounts of from about 0.1 to 10% by weight, relative to the sum of the liquid phases water and oil. Preferred amounts are within the range of from about 0.5 to 5% by weight of the emulsifier components, while the range of from about 1 to 3% by weight of the emulsifier - again relative to the sum of water + oil - is of particular importance.

Within the scope of the so far known preparation of surface-active alkyl glycoside compounds it is desired that the alcohol employed in an excessive amount in the acetalization reaction is separated from the product of the acetalization to such an extent that at best a few percent of free alcohol would remain in the reaction mixture. Reference is made to the corresponding information set forth in the DE-A1 38 33 780 and the

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method described therein to attain said purpose by thin film evaporation for recovering the alcohol. Operating in accordance with the invention will not require said comparably expensive process step. The alcohols R-OH employed for the acetalization throughout are oleophilic alcohol components which are present in an excessive amount and in admixture with the alkyl glycoside formed or may be supplied to the intended use. If desired, the excess amount of alcohol may be partially removed while, however, in a preferred embodiment of the invention it is provided to employ the alkyl glycosides together with at least about 50% by mole and preferably together with about 100% by mole of free alcohol - % by mole in each case relative to alkyl glycoside compound. The economical production of the emulsifiers according to the invention is further facilitated by omitting the step of bleaching the reaction products as primarily obtained, which step in prior art as evidenced by the pertinent printed publications is considered as an essential process step. Thus, the production process for compositions of active substances containing alkyl glycoside compounds within the scope of the invention may be restricted to the process step of acetalization - expediently in the presence of acidic catalyst. The crude reaction product may be directly put into a commercial use.

As to the forms of the alkyl glycosides for handling in practice, two essentially anhydrous formulations have proven to be useful: For one, the alkyl glycosides may be stored and handled as concentrated solutions in preferably ecologically acceptable oil phases. On the other hand, it is possible to employ the alkyl glycosides as solids - here especially as granules. Since the

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emulsifier compounds as such, although they are usually solids, tend to sticking and/or smearing, it may be appropriate to additionally use particulate solids in the formation of the respective granules. Here typical auxiliary materials used in crude oil technology and particulate in nature are suitable, for example weighting agents, salts, viscosity builders and the like, or inert auxiliary materials may be included in the use.

In the preferred embodiment as especially featured in the introduction, the appropriate oil phases are constituted by the ecologically compatible ester oils, oleophilic alcohols and/or ethers described in applicant's older applications as quoted. When said agents are used, the invention relates to the drill-hole treatment agents which are fluid and pumpable within the temperature range of from 5 °C to 20 °C, and more specifically drilling fluids based on

- either a continuous oil phase, especially in admixture with a dispersed aqueous phase (W/O inverted type)
- or a dispersed oil phase in a continuous aqueous phase (O/W emulsion type).

The ecologically compatible oils and oil phases, with respect to the possible physical properties thereof, cover a wide range. The invention comprises, on the one hand, oil phases which are fluid and pumpable also at low temperatures. These, more particularly, include representatives suitable for the preparation of W/O emulsions. However, on the other hand, highly viscous to solid oil phases and materials of this type may also be included in the use within the scope of the teaching according to the invention. This may be exemplified by the following deliberations:

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For water-based O/W emulsion fluids a high mobility of the dispersed oil phase is not required and, as the case may be, not even desirable. For example, to ensure good lubricating properties, oil phases adjusted such as to be comparably viscous may be advantageous. Another possible use of highly viscous or even solid ecologically compatible oil phases may be constituted, if the respective oil phase involved in the final product is only partially formed by said highly viscous to solid representatives of degradable esters, alcohols and/or ethers which themselves have been admixed with comparably highly liquid oils of this kind.

Nevertheless, there is consistently applicable to all oil phases or mixed oil phases to be used according to the invention that flash points of at least about 100 °C and preferably flash points of above about 135 °C are demanded for reasons of safety in operations. Values that are distinctly higher, particularly those above 150 °C, may be especially expedient. Furthermore, there is consistently applicable to the oil phases as potentially susceptible to hydrolysis that may be used within the scope of the invention not only that the requirement of the ecological compatibility will have to be met by the compound put into use, i.e., for example, the respectively selected ester oil or ester oil mixture, but also that no toxicological and especially no inhalation-toxicological danger will be induced upon a partial saponification in practical use. Within the scope of the mentioned older applications there has been described in great detail that here, more particularly, the various representatives of ester oils are referred to, with the monofunctional alcohols from the esters formed being again of particular significance here. In

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comparison to polyfunctional alcohols, the lower members of the monofunctional alcohols are highly volatile, so that here a partial hydrolysis may cause exposure to secondary danger. Accordingly, in the classes of the various ester oils those monofunctional alcohols included in the use, or the moieties of such alcohols, have been chosen so that they have at least 6 carbon atoms, and preferably at least 8 carbon atoms, in the molecule thereof.

The inverted drilling fluids of the kind involved according to the invention, irrespectively of a definite property of the continuous oil phase, in preferred embodiments have a plastic viscosity (PV) within the range of from 10 to 60 mPa.s and a flow limit (yield point, YP) within the range of from 5 to 40 lb/100 ft² - each determined at 50 °C.

As an oil phase which is ecologically compatible and well fluid at low temperature, there have proven to be useful, more specifically, ester oils of monocarboxylic acids which then, in a preferred embodiment of the invention, are derived from at least one of the following subclasses:

- a) Esters of C₁₋₅-monocarboxylic acids and mono- and/or polyfunctional alcohols, whereof the moieties of monohydric alcohols comprise at least 6 carbon atoms and preferably at least 8 carbon atoms and the polyhydric alcohols preferably have from 2 to 6 carbon atoms in the molecule,
- b) Esters of monocarboxylic acids of synthetic and/or natural origin comprising from 6 to 16 carbon

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atoms, and more specifically esters of aliphatic saturated monocarboxylic acids and mono- and/or polyfunctional alcohols of the kind mentioned in a),

- c) Esters of olefinically mono- and/or polyunsaturated monocarboxylic acids having at least 16, and especially 16 to 24 carbon atoms and especially monofunctional straight-chain and/or branched alcohols.

Starting materials for recovering numerous monocarboxylic acids falling under these subclasses, especially those having a higher number of carbon atoms, are vegetable and/or animal oils. There may be mentioned coconut oil, palm kernel oil and/or babassu oil, especially as feedstock for the recovery of monocarboxylic acids of the prevailing range up to C_{18} and of essentially saturated components. Ester oils of vegetable origin based on olefinically mono- and optionally poly-unsaturated carboxylic acids of the range of C_{16-24} are, for example, palm kernel oil, peanut oil, castor oil, sunflower oil, and especially rapeseed oil. But also components synthetically recovered are important structural elements for ecologically compatible oil phases on the side of the carboxylic acids as well as on the side of the alcohols.

Preferably, the oil phase has a solidification of below about 0°C and a Brookfield Viscosity at zero to 5°C of less than about 55 mPa.s.

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Additives to the oil-based and/or water-based fluid

Inverted drilling muds conventionally contain, together with the continuous oil phase, the finely dispersed aqueous phase in amounts of from 5 to 50% by weight. In water-based emulsion fluids the dispersed

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oil phase is usually present in amounts of from at least about 1 to 2% by weight, frequently in amounts of from at least about 5% by weight with an upper limit of the oil portion of about from 40 to 50% by weight - the percentage by weight in all cases being based on the sum of the unloaded liquid portions of oil/water.

Besides the water content, there are to be taken into consideration all of the additives provided for comparable types of fluids. Said additives may be water-soluble, oil-soluble and/or water-dispersible and/or oil-dispersible.

Conventional additives, besides the emulsifiers defined according to the invention, include, for example, fluid-loss additives, soluble and/or insoluble materials to build-up structural viscosity, alkali reserve, agents for inhibiting an undesirable water exchange between drilled formations - e.g. water-swellable clays and/or salt layers - and the, e.g., water-based drilling fluid, wetting agents for an improved strike of the emulsified oil phase on solid surfaces, e.g. for improving the lubricating effect, but also for improving the oleophilic closure of exposed rock formations, e.g. rock surfaces, biocides, for example for inhibiting bacterial onset and growth of O/W emulsions and the like. In detail, reference is here to be made to pertinent prior art such as described, for example, in the technical literature as initially quoted; cf., more specifically, Gray and Darley, loc. cit., Chapter 11, "Drilling Fluid Components". Just by way of an excerpt, there may be quoted:

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Finely dispersed additives for increasing the density of the fluid: Widely used is barium sulfate (baryte), but also calcium carbonate (calcite) or the mixed carbonate of calcium and magnesium (dolomite) are used.

Agents for a build-up of structural viscosity which simultaneously will act as fluid-loss additives: Here, bentonite or hydrophobized bentonite are to be mentioned in the first place. For salt water fluids, other comparable clays, and more specifically attapulgite and sepiolite are of considerable importance in practice.

Also the use in combination of organic polymer compounds of natural and/or synthetic origin may be of considerable importance in this connection. There may be especially mentioned starch or chemically modified starches, cellulose derivatives such as carboxymethyl-cellulose, guar gum, xanthan gum, or also merely synthetic water-soluble and/or water-dispersible polymer compounds, especially of the type of the high molecular weight polyacryl amide components with or without anionic or cation modifications, respectively.

Diluents for regulating the viscosity: The so-called diluents (thinners) may be organic or inorganic in nature. Examples for organic thinners are tannin and/or quebracho extract. Further examples are lignite and lignite derivatives, especially lignosulfonates. However, as has been set forth hereinabove, in a preferred embodiment, just here no toxic compounds will be included in the use, among which in the first place the respective salts with toxic heavy metals such as chromium and copper are to be mentioned. Polyphosphate

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compounds constitute an example of inorganic thinners.

Additives inhibiting the undesirable water-exchange with, for example, clays: Here to be considered are the additives known from prior art for oil- and water-based drilling fluids. These include halides and/or carbonates of the alkali and/or alkaline earth metals, whereof the potassium salts, optionally in combination with lime, may be of particular importance.

Reference may be made, for example, to the relevant publications in "Petroleum Engineer International", September 1987, 32-40, and "World Oil", November 1983, 93-97.

Alkali reserves: Here to be taken into consideration are inorganic and/or organic bases adjusted to match the total behavior of the fluid, and more particularly basic salts or hydroxides of alkali and/or alkaline earth metals as well as organic bases. Kind and amount of these basic components will have been selected and mutually adjusted in a known manner so that the drilling hole treating agents will be adjusted to a pH value within the range of from about neutral to moderately basic, especially to the range of from about 7.5 to 11.

Basically, the amounts of each of the auxiliary materials and additives is within the conventional range and, thus, may be learnt from the relevant literature as quoted.

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E X A M P L E S

In the following Examples 1 to 4, by observation of a standard formulation for oil-based drilling fluid systems of the W/O type there are set forth appropriate drilling fluid systems, wherein each continuous oil phase is formed by a selected oleophilic carboxylic acid ester of the following definition:

An ester mixture comprising substantially saturated fatty acids based on palm kernel and 2-ethylhexanol which to the by far predominating part is derived from C_{12/14}-carboxylic acids and conforms to the following specification:

C₈: from 3.5 to 4.5% by weight
C₁₀: from 3.5 to 4.5% by weight
C₁₂: from 65 to 70 % by weight
C₁₄: from 20 to 24 % by weight
C₁₆: about 2 % by weight
C₁₈: from 0.3 to 1 % by weight

The ester mixture is a bright yellow liquid which has a flash point in excess of 165 °C and a viscosity (Brookfield, 20 °C) of from 7 to 9 cP.

The viscosity characteristics are determined with unaged and aged material as follows:

Measurement of the viscosity at 50 °C in a Fann-35-viscosimeter from the company Baroid Drilling Fluids, Inc.. In a per se known manner there have been determined the plastic viscosity (PV), the yield point (YP) and the gel strength (lb/100 ft²) after 10 seconds and after 10 minutes. In Example 1 there is further determined the fluid loss value (HTHP).

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Ageing of the respective drilling fluid is effected by way of a treatment at 125 °C in an autoclave - in a so-called roller oven - for 16 hours.

The drilling fluid systems are composed in a per se known manner in accordance with the following basic formulation:

230	ml of carboxylic acid ester oil
26	ml of water
6	g of organophilic bentonite (GELTONE TM from the company Baroid Drilling Fluids, Inc.)
12	g of organophilic lignite (DURATONE TM from the company Baroid Drilling Fluids, Inc.)
2	g of lime
6	g of emulsifier based on alkyl glycoside
3	g of co-emulsifier based on C ₁₈ fatty acid - only used in Examples 3 and 4 -
346	g of baryte
9.2	g of CaCl ₂ . 2 H ₂ O

Example 1

As an emulsifier based on alkyl glycoside there is employed the condensation product of glucose and C₁₆-fatty alcohol of natural origin (commercial product "Lorol C₁₆"TM of applicant). The characteristic values - as indicated above - determined of the unaged and of the aged materials have been compiled in the following summarizing Table.

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	Unaged Material	Aged Material
Plastic viscosity (PV)	41	44
Yield point (YP)	14	22
Gel strength (lb/100 ft ²)		
10 seconds	7	18
10 minutes	11	36

HTHP 3 ml

Example 2

In this Example there is employed, as an emulsifier based on alkyl glycoside, the reaction product of glucose with a fatty alcohol mixture of natural origin with a by far prevailing chain length of C₁₂₋₁₄ (commercial product "LorolTM 1214" of applicant). The characteristic values determined of the unaged and of the aged materials are as follows:

	Unaged Material	Aged Material
Plastic viscosity (PV)	41	42
Yield point (YP)	15	18
Gel strength (lb/100 ft ²)		
10 seconds	8	13
10 minutes	11	25

HTHP 5 ml

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Example 3

The run of Example 1 is repeated, except that - as initially indicated - a co-emulsifier based on C₁₈-fatty acid is additionally employed. The characteristic values determined of the unaged and of the aged materials are as follows:

	Unaged Material	Aged Material
Plastic viscosity (PV)	37	36
Yield point (YP)	7	8
Gel strength (lb/100 ft ²)		
10 seconds	5	6
10 minutes	11	5

Example 4

The run of Example 2 is repeated, except that also here a co-emulsifier based on C₁₈-fatty acid is additionally employed. The characteristic values determined of the unaged and of the aged materials are as follows:

	Unaged Material	Aged Material
Plastic viscosity (PV)	38	35
Yield point (YP)	13	10
Gel strength (lb/100 ft ²)		
10 seconds	7	5
10 minutes	14	9

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Example 5

In the following Example 5 a water-based emulsion fluid using a complex oleophilic polycarboxylic acid ester having lubricating properties is prepared as a dispersed oil phase in accordance with the following procedure:

First, a homogenized slurry containing 6% by weight of bentonite is produced from a commercially available bentonite (non-hydrophobized) and tap water and the pH value thereof is adjusted to from 9.2 to 9.3 with caustic soda solution.

This pre-swollen bentonite phase is charged and, in subsequent process steps - each with thorough mixing - , the individual components of the water-based ester-oil emulsion are incorporated in accordance with the following formulation:

350	g	of 6% by weight bentonite solution.
1.5	g	of commercial carboxymethylcellulose (of low viscosity) (Relatin U 300 S 9)
35	g	of sodium chloride
70	g	of complex ester
3	g	of emulsifier of Example 2
219	g	of baryte

As an oleophilic ester oil phase there is employed the reaction product of trimethylolpropane (14% by weight), a commercially available dimer fatty acid mixture (24% by weight) and oleic acid as the balance. The dimer fatty acid mixture contains 77% by weight of dimer acids and tri- and higher polycarboxylic acids as the balance - here % by weight relative to the dimer fatty acid mixture.

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The viscosity of the O/W emulsion fluid thus prepared is determined as follows:

First the plastic viscosity (PV), the yield point (YP) and the gel strength after 10 seconds and 10 minutes of the unaged emulsion fluid are determined at room temperature.

Then the emulsion fluid is aged under static conditions at 90 °C for 16 hours in order to test the influence of the temperature on the stability of the emulsion. Then the viscosity values are once more determined at room temperature.

	Unaged Material	Aged Material
Plastic viscosity (PV)	18	16
Yield point (YP)	101	114
Gel strength (lb/100 ft ²)		
10 seconds	49	52
10 minutes	50	53

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CLAIMS:

1. An invert emulsion drilling fluid composition suitable for the environmentally-acceptable development of a geological resource, said composition comprising;
 - (a) an ecologically-compatible continuous oil phase;
 - (b) an aqueous phase dispersed in said oil phase;
 - (c) a thickening agent;
 - (d) a fluid-loss additive;
 - (e) a weighting agent;
 - (f) an alkali reserve component; and
 - (g) a water-in-oil emulsifier component comprising a surface-active alkyl glycoside.
2. A composition as in claim 1, wherein said alkyl glycoside has the structural formula I:
$$R - O - Z_n \quad (I)$$
wherein:

R represents a linear or branched, saturated or unsaturated alkyl radical containing at least 8 carbon atoms;

Z represents one or more aldose or ketose units; and

n has an average value of 1 to 5.
3. A composition as in claim 2, wherein R contains at least 12 carbon atoms and n has a maximum value of 2.
4. A composition as in claim 1, 2 or 3, wherein said alkyl glycoside is present in the amount of about 0.1 to about 10% by weight, based on the sum of the weight of said oil phase and said aqueous phase.

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5. A composition as in any one of claims 1 to 4, wherein said oil phase is selected from the group consisting of an ester oil of a mono- or polycarboxylic acid and a mono- or polyfunctional alcohol, a carbonic acid ester oil, an oleophilic alcohol and an oleophilic ether.

6. A composition as in claim 5, wherein said ester oil of a mono- or polycarboxylic acid and a mono- or polyfunctional alcohol is selected from the group consisting of:

a) an ester of a C_1 - C_6 monocarboxylic acid and a mono- or polyfunctional alcohol wherein said monofunctional alcohol contains at least 6 carbon atoms and said polyfunctional alcohol contains from 2 to 6 carbon atoms in the molecule;

b) an ester of a C_6 - C_{16} aliphatically saturated monocarboxylic acid and a mono- or polyfunctional alcohol as in a); and

c) an ester of a mono- or polyolefinically unsaturated C_{16} - C_{24} monocarboxylic acid and a monofunctional straight chain or branched alcohol.

7. A composition as in any one of claims 1 to 6, wherein said oil phase has a flash point of at least about 100°C.

8. A composition as in any one of claims 1 to 7, wherein said oil phase has a solidification value of below about 0°C and a Brookfield viscosity at 0 to 5°C of less than about 55 mPa.s.

9. A composition as in any one of claims 1 to 8, having a plastic viscosity of from about 10 to about 60 mPa.s and a yield point of from about 5 to about 40 lbs/100 ft², each determined at about 50°C.

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10. A composition as in any one of claims 1 to 9, wherein said aqueous phase comprises from about 5 to about 50% by weight of said composition, and contains CaCl_2 or KCl salts dissolved therein.

11. A composition as in any one of claims 1 to 10, wherein said geological resource is an oil or natural gas deposit.

12. A process of developing a geological resource by drilling, comprising contacting said resource during drilling with an ecologically-acceptable composition as in any one of claims 1 to 11.



SPE 53941

A New High-Temperature Oil-Based Drilling Fluid

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Abstract

This paper presents the laboratory development and a field trial of a novel 100% oil base drilling fluid system. In response to the need for a competitive high temperature inhibitive system, lab testing found an oil soluble polymer that imparts high temperature high pressure fluid loss control in a mud system with stable rheology and low formation damage. The polymeric additive is the basis for the 100% oil system, which also has an application in standard invert emulsion systems. The 100% oil system is designed to use mineral or diesel oil as the base. The attributes of the system include inherent inhibition and lubricity from the base oil, a mud weight range of 7.0-18.0 ppg, minimal formation damage, resistance to contamination and maintenance of the HPHT filtration control and rheology during high temperature high pressure applications. Laboratory testing has shown the fluid is temperature stable to 400 °F with diesel or low toxicity mineral oil as the base.

This system has been field tested on two wells in Eastern Venezuela. One test was a 6,353', 8 1/2" directional interval and the other a 1,053', 5 7/8" horizontal section drilled in near balance conditions with the fluid being nitrogenated to achieve the desired ECD. Both wells were drilled successfully and one well is discussed in this report.

This fluid has a wide range of applications evidenced by the documented properties from the lab and the field tests. This paper covers the system formulations, properties, formation damage tests, and the results from the field test.

Introduction

The drilling of deep wells worldwide requires a continued search for drilling fluids capable of withstanding very high temperatures and pressures^{1,4}. In Venezuela, the deep drilling performed in the Eastern zone of the country and in Maracaibo Lake require high temperature high pressure fluids.

Oil based drilling fluids have definite advantages when compared to water based fluids. These include maintaining stable rheology and filtration control for extended periods of time and increased lubricity. In addition, oil base drilling fluids can be used to drill through most troublesome shale formations due to their inherent inhibitive nature and temperature stability⁵⁻⁷.

On the other hand, the utilization of diesel as the base oil in these fluids brings about many environmental concerns^{8,9}. Environmental conservation issues worldwide and in Venezuela are increasing every year leading to stricter regulations designed to protect sensitive areas. These laws cover the entire drilling fluid process such as the type of drilling fluid to be used, its environmental effect, toxicity, biodegradability, cuttings handling and bioremediation. However, most commercial oil base drilling fluid systems have limitations such as reduced rheology and filtration control if the fluid is exposed to temperatures higher than 300 °F (149 °C) for prolonged periods of time¹.

PDVSA-INTEVEP studied and evaluated commercially available oil base drilling fluids and developed a new oil base system named INTOIL™ as a result of the work. The system is formulated to cover a wide density range (7-18 ppg) and is stable after prolonged exposure to 400 °F. This new oil base drilling fluid is an alternative fluid suitable for drilling shallow, intermediate and deep wells.

The utilization of a polymeric additive allowed for the development of two versions of the system. The first is 100 % oil and the second is an invert emulsion. Both have lower solids contents than commercially available oil base fluids, are capable of withstanding high temperatures and pressures and can be formulated using diesel or a low toxicity mineral oil. The INTOIL™ system may be used in environmentally

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sensitive areas when low toxicity mineral oil is the base of the fluid¹⁰.

The 100 % oil system is composed of an oil-soluble polymer, organophilic clay, a primary emulsifier, lime, and a weighting agent, and. This formulation has stable rheological properties and fluid loss control after aging at 400 °F for 16 hrs. The invert emulsion contains the oil-soluble polymer, an emulsifier, a brine phase, lime, and weighting agent and is stable at 350 °F. It is worth mentioning that this emulsion has stable rheological properties without the need for an organophilic clay.

This paper presents laboratory test results and the first field trial of the 100% oil version of the system with mineral oil as the base. The fluid was used for drilling the 8 1/2" section of Coporo-12 well, (Coporo field, Edo. Guárico, Venezuela), with an estimated BHT of 220 °F. Coporo-12 was a deviated well with a kick off point at 1,501'. Drilling with this fluid began at 607' and reached a Cretaceous objective at 6,980' (RS-129 sand). The density range was 9.1 ppg to 10.4 ppg.

Formulation

INTOIL™ 100 % oil system

The 100 % oil system contains a polymeric additive that imparts high temperature high pressure fluid loss, an organophilic clay, an emulsifier for stabilizing possible water contamination and a weighting agent (calcium carbonate, barite or hematite). Table 1 shows average concentrations of the additives for different density and temperature ranges.

Tables 2-8 present the fluid properties of the 100 % oil system for a range of densities and temperatures using a low toxicity mineral oil as the base. The results show that the system maintains stable properties at 400 °F.

The rheological properties have a strong correlation to the polymer/organophilic clay ratio, organophilic clay type and wetting and weighting agent used. Lab results show that the polymer has a strong influence on the organophilic clay behavior when mineral oil is the base because the absence of aromatic compounds does not allow organophilic clay to yield properly¹¹⁻¹³. When the polymer is used in conjunction with the organophilic clay, there is a characteristic spatial arrangement caused by the interaction of polymeric chains with organophilic clay platelets. The rheological properties of this system are equivalent to those of an oil based fluid with organophilic clay activated by water or any other polar activator. It is worth mentioning that depending on the polymer/organophilic clay ratio, different behavior is observed varying between a system with low and high rheological properties. This situation is similar to the action of acrylamide copolymers used in water based fluids¹⁴.

Rheological properties increase progressively at increased solids content levels (in particular the plastic viscosity), and vary according to the specific gravity of the weighting agent.

For densities between 9 ppg and 12 ppg, a blend of calcium carbonate and barite is recommended instead of calcium carbonate alone to avoid undesirable high rheology. For densities in the 15 ppg range, barite or hematite can be used, whereas for densities approaching 18 ppg, hematite is the most suitable weight material.

In all the cases, the high temperature high pressure fluid loss results are very low. The polymer/organophilic clay interaction produces a thin, flexible and durable filter cake by ordering the clay platelets through polymeric bridging. This arrangement is less porous than that produced by the organophilic clay alone.

The use of a non-ionic wetting agent in place of a primary anionic emulsifier also affects the rheological properties of the INTOIL™ system. An increase in rheological properties after aging is observed when the non-ionic wetting agent is used in place of the lime-activated, primary anionic emulsifier, at the same concentration. The result of using the wetting agent in place of the emulsifier increases the wettability of the organophilic clay by the base oil. When this wetting agent is combined with the polymer and the organophilic clay, an increase of the rheological properties of the fluid can be observed due to a synergetic effect between these three components.

In addition, it is important to mention that 5% formation damage was obtained for a formulation containing 5 ppb of polymer that was 9.0 ppg.

INTOIL™ invert emulsion system

A notable feature of the invert emulsion is the lack of organophilic clay in the formulation to achieve stable and desirable rheological properties. Table 9 shows the average product concentrations of the additives and a description of each. Table 10 includes a range of formulations and the resulting properties with varying densities and temperatures (300 °F and 350 °F) using a low toxicity mineral oil as the base fluid. The tables show that the system has stable rheology and fluid loss control after aging at 350 °F.

Field application

The 100 % oil INTOIL™ system was used to drill the 8 1/2" section of the well Coporo-12, located in Coporo field, Edo. Guárico, Venezuela. This field is assigned to Teikoku Oil of Venezuela. The Chaguaramas, Roblecito and La Pascua formations were drilled, and the casing was set in the Cretaceous section. The target was the RS-129 sand. Coporo-12 was planned as a directional well, with a kick off point at 1501' (MD), with an inclination of 24.9° in the N16.35°E direction, up to the estimated depth of 6,707'. TVD was 6,000', and BHT was approximately 220 °F.

Figure 1 shows a diagram of Coporo-12 well which includes the formations drilled as well as the corresponding

mud weights. Tables 11-13 present the initial formulation of the system, and the initial and average fluid properties.

While drilling with this system, initial ROP was 143 ft/hr with a pump rate of 417 gpm up to the kick off point at 1,501'. Drilling continued without problems to 2,957' with an average ROP of 140 to 180 ft/hr, reaching instantaneous ROP's of 280 ft/hr. Good hole cleaning was observed and no treatment was required except for additions of calcium carbonate to increase the mud weight to 9.3 ppg. At 2,994' a 30 % by volume water intrusion was encountered and controlled by pumping a 10.7 ppg calcium carbonate pill. In addition, the fluid was treated and conditioned to reduce the water concentration to 14 % by volume and the mud weight was increased to 9.6 ppg. Drilling resumed with a water content of 6 %, and a ROP of 40 ft/hr until drilling to 3,480'. At 3,950', the density was increased again for hole stability. Drilling continued with a ROP of 27 ft/hr. to 4,438' where the mud weight was increased to 10.3 ppg. Drilling continued to 6,707' with a water content of 2 %. Table 14 shows the properties of the system as a function of depth and Figures 2-5 show the variation of the rheological properties and filtration control while drilling. The fluid maintained excellent properties during the whole course of the operation, tolerated 14 % by volume water contamination and 25 % by volume solids without being adversely affected.

Conclusions

1. The INTOIL™ system can be formulated for a wide range of densities (7-18 ppg) for the 100 % oil system and the invert emulsion.
2. The INTOIL™ system which is 100 % oil has stable flow properties and high temperature high pressure fluid loss control at 400 °F.
3. The INTOIL™ invert emulsion has stable rheology and filtration control up to 350 °F.
4. The INTOIL™ invert emulsion does not need organophilic clay in the formulation for keeping solids in suspension.
5. The INTOIL™ system which is 100% oil performed very well during the whole course of the drilling operation of Coporo-12 well. Very high average and instantaneous ROP's (180 ft/hr and 280 ft/hr, respectively) were reached.
6. The fluid is capable of tolerating a water contamination of 14 % by volume without losing the rheological or fluid loss control properties.
7. The fluid is capable of tolerating a solids content of 25 % by volume, without an undesirable plastic viscosity increase.

Acknowledgements

We thank Mr. Javier Espinoza for the excellent work performed in the laboratory; Mr. José Blanco for his assistance in the commercialization of the INTOIL™ fluid; Drilling Fluids Business for supporting the development of INTOIL™ (PDVSA Intevep); Teikoku Oil de Venezuela for utilizing INTOIL™ in the well Coporo-12; BHI personnel for their confidence in INTOIL™.

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SI Metric Conversion Factors

cP × 1.0*	E - 03 = Pa
ft × 3.048*	E - 01 = m
ft ² × 9.290 304*	E - 02 = m ²
ft ³ × 2.831 685	E - 02 = m ³
in. × 2.54*	E - 00 = cm
lbf × 4.448 222	E - 00 = N
md × 9.869 233	E - 04 = μ m ²
psi × 6.894 757	E - 00 = kPa

* Conversion factor is exact.

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TABLE 1. STANDARD FORMULATION FOR THE 100 % OIL INTOIL™ DRILLING FLUID

ADDITIVE	FUNCTION	CONCENTRATION
OIL (GASOIL OR MINERAL OIL)	BASE OIL	AS NEEDED
POLYMERIC ADDITIVE	HPHT FLUID LOSS CONTROL AGENT	2-6 ppb
ORGANOPHILIC BENTONITE/HECTORITE	VISCOSIFIER	2-12 ppb
EMULSIFIER OR WETTING AGENT	EMULSIFIES WATER IN CASE OF CONTAMINATION/ IMPROVES OIL-WETTING OF THE WEIGHTING AGENT	2-6 ppb
LIME	REACTS WITH THE EMULSIFIER IN PRESENCE OF WATER IN CASE OF WATER CONTAMINATION	4-10 ppb
WEIGHTING AGENT	HOLE STABILITY	AS NEEDED

TABLE 2. INTOIL™ 100 % OIL FORMULATIONS USING MINERAL OIL, DENSITY: 9 ppg

ADDITIVES	F1	F2	F3	F4	F5	F6	F7	F8
MINERAL OIL (bbls)	0.922	0.922	0.922	0.922	0.860	0.860	0.911	0.911
POLYMERIC ADDITIVE (ppb)	4	5	4	5	4	5	4	4
ORGANOPHILIC BENTONITE (ppb)	12	12	12	12	12	12	10	12
EMULSIFIER (ppb)	6	6	6	6	6	6	6	6
LIME (ppb)	4	4	10	10	10	10	10	10
CALCIUM CARBONATE (ppb)	--	--	--	--	130.6	130.6	50	50
BARITE (ppb)	114.75	114.75	114.75	114.75	--	--	69.8	69.8
AGING TEMPERATURE (°F), 16 HRS	250	250	250	250	250 300	250 300	250 300	250 300
PLASTIC VISCOSITY (cP) @ 150 °F *	19/26	30/33	31/27	33/38	49/40 10/13	37/34 40/41	24/23 24/19	26/26 28/23
YIELD POINT (lb/100 ft²)	8/11	9/22	12/15	16/20	35/36 9/7	23/17 25/31	10/7 10/6	11/10 13/14
L6 (lb/100 ft²)	3/5	3/6	5/6	7/7	34/38 11/14	8/10 10/11	5/4 5/4	6/6 6/5
L3 (lb/100 ft²)	2/4	2/5	4/5	6/6	21/15 10/7	7/9 9/10	4/3 4/3	5/5 5/4
GEL 10" (lb/100 ft²)	2/4	2/5	5/6	6/7	12/16 15/20	7/9 9/11	4/4 4/4	5/5 5/5
GEL 10' (lb/100 ft²)	3/7	3/10	7/10	9/12	11/9 13/10	10/12 12/14	7/7 7/6	7/8 8/10
HPHT FILTRATE VOLUME AT AGING TEMPERATURE AFTER AGING (ml/30 min)	3.0	2.0	3.5	3.0	1.0 4.0	4.0 3.0	3.0 3.0	2.5 2.0

* The properties before and after aging are separated by a slash (/).

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(40) 08.04.2003

(43) 20.02.1992

(45) 08.04.2003

(12)

(21) 2 088 697

(51) Int. Cl.⁸: **C09K 7/06, C09K 7/02,
B01F 17/56**

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(86) PCT/EP91/01396

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(30) **P 40 24 658.2 DE 03.08.1990**

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(54) **UTILISATION DE COMPOSES TENSIO-ACTIFS A BASE DE GLYCOSIDE ALKYLE DANS DES FLUIDES DE
FORAGE A BASE D'EAU ET D'HUILE ET AUTRES AGENTS DE TRAITEMENT POUR PUITS DE FORAGE
(54) USE OF SURFACE-ACTIVE ALKYL GLYCOSIDE COMPOUNDS IN WATER- AND OIL-BASED DRILLING
FLUIDS AND OTHER DRILL-HOLE TREATMENT AGENTS**

(57)

Described is the use of surface-active alkyl glycoside compounds as ecologically compatible emulsifiers of the W/O type and O/W type, respectively, in fluid and pumpable drilling fluids and other fluid drilling-hole treatment agents which comprise a continuous or a dispersed oil phase together with an aqueous phase and which are suitable for an environment-ally acceptable exploitation of geological resources, for example oil or natural gas deposits. The invention further relates to inverted drilling fluids which are suitable for a non-polluting exploitation of geological resources and contain a continuous oil phase and, present therein, a dispersed aqueous phase together with emulsifiers, further conventional auxiliary agents such as thickeners, fluid-loss additives, weighting agents, water-soluble salts and/or alkali reserves, said inverted drilling fluids being characterized in that they contain surface-active alkyl glycoside compounds of formula (I) as emulsifier or as an emulsifier component together with an ecologically compatible continuous oil phase.

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50028-0034

10/28/05

IN THE UNITED STATES DISTRICT COURT
FOR THE EASTERN DISTRICT OF TEXAS
TYLER DIVISION

HALLIBURTON ENERGY SERVICES,
INC.,

Plaintiff,

v.

M-I, L.L.C.,

Defendant.

CIVIL ACTION NO. 6:05-CV-155(LED)

Jury Demanded

M-I, L.L.C.'S PRELIMINARY INVALIDITY CONTENTIONS

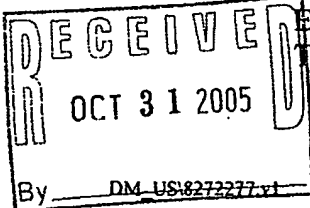
Plaintiff Halliburton Energy Services, Inc. ("Halliburton"), pursuant to its Complaint and Disclosure of Asserted Claims and Preliminary Infringement Contentions as required by P.R. 3-1, has asserted that M-I, L.L.C.'s ("M-I's") Rheliant drilling fluid system infringes, contributes to infringement, or induces infringement of claims 1-3, 5-6, 8-24, 33, 39-40, 42-43, 45-62, 71, 77-78, 80-81, 83-99, 108, 114-115, 117-118, 121, 123-131, 140, 146-147, and 149-150 of U.S. Patent No. 6,887,832 ("the '832 patent"). In addition, in separate correspondence Halliburton confirmed that the priority date assignable to each and every asserted claim is the '832 patent application filing date: June 19, 2002.

In response and pursuant to P.R. 3-3, M-I provides its Preliminary Invalidity Contentions as follows:

(a) **Identity of Prior Art Items:**

- 35 U.S.C. §§ 102(a), 102(b), and/or 103(a) – publications

(A) Kim Burrows et al., "New Low Viscosity Ester Is Suitable for Drilling Fluids in Deepwater Applications," SPE/IADC 66553, presented at the SPE/EPA/DOE Exploration and Production Environmental Conference held in San Antonio, Texas, Feb. 26-28, 2001.



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- (B) Baroid Drilling Fluids PETROFREE Biodegradable Invert Emulsion Drilling Fluid (1993) & RM-63 Rheology Modifier (1990) product brochures.
- (C) United States Patent No. 5,237,080, which issued on August 17, 1993 and includes earlier publication priority data on its face.
- (D) United States Patent No. 6,289,989, which issued on September 18, 2001 and includes earlier publication priority data on its face.
- (E) United States Patent No. 5,254,531, which issued on October 19, 1993.
- (F) United States Patent No. 5,441,927, "Fluid Drill-Hole Treatment Agents Based on Polycarboxylic Acid Diesters," which issued on August 15, 1995 and includes earlier publication priority data on its face.
- (G) L. Knox et al., "New Developments in Ester-based Mud Technology," AADE-02-DFWM-HO-41, presented at the AADE 2002 Technology Conference held in Houston, Texas, Apr. 2-3, 2002.
- (H) L.J. Fraser, "Field Application of the All-Oil Drilling Fluid Concept," IADC/SPE 19955, presented at the 1990 IADC/SPE Drilling Conference held in Houston, Texas, Feb. 27-Mar. 2, 1990.
- (I) Transcript of Designated Confidential Oral Deposition of Kimberly Burrows, Oct. 26, 2005 ("Burrows Tr.").
- (J) International Application No. PCT/GB95/00680 (International Publication No. WO 95/26386), entitled "Drilling Mud," which published on October 5, 1995 and includes earlier publication priority data on its face.
- (K) Canadian Patent No. 2,088,697, which issued on April 8, 2003, but contains earlier publication priority data on its face indicating a publication date of February 20, 1992.
- (L) C. Cameron, "Drilling Fluid Design and Management for Extended Reach Drilling," IADC/SPE 72290, presented at the IADC/SPE Middle East Drilling Technology meeting held in Bahrain, Oct. 22-24, 2001.
- (M) Daniel Eckhout et al., "Development Process and Field Applications of a New Ester-based Mud System for ERD Wells on Australia's Northwest Shelf," IADC/SPE 62791, presented at the 2000 IADC/SPE Asia Pacific Drilling Technology meeting held in Kuala Lumpur, Malaysia, Sept. 11-13, 2000.
- (N) Luigi F. Nicora et al., "High-Density Invert-Emulsion System with Very Low Solids Content to Drill ERD and HPHT Wells," SPE 65000, presented at the 2001

SPE International Symposium on Oilfield Chemistry held in Houston, Texas, Feb. 13-16, 2001.

- (O) M. Mas et al., "A New High-Temperature Oil-Based Drilling Fluid," SPE 53941, presented at the 1999 SPE Latin American and Caribbean Petroleum Engineering Conference held in Caracas, Venezuela, Apr. 21-23, 1999.
- (P) International Application No. PCT/US96/0093 (International Publication No. WO 96/22342, entitled "Base Oil for Wellbore Fluids," which published on July 25, 1996.

- **35 U.S.C. § 102(b) – on sale bar**

- (Q) Petrofree LV drilling fluid system, including thinners Coldtrol, ATC, and OMC-42, was sold by Halliburton to Kerr-McGee Corporation in 1999 or 2000 in combination with an invert emulsion base, thinners, emulsifiers and weighting agents. (See Prior Art Item (A); HAL0015101-15103, HAL 0015053-0015071; Burrows Tr. at p. 61 l. 3 to p. 62 l. 5, p. 86 l. 25 to p. 88 l. 10.)

In addition, Petrofree (ester based oil), Petrofree SF (internal olefin base oil), Petrofree LV (low-viscosity ester base oil), and Petrofree LE (linear alpha olefin base oil) were all available prior to June of 2001 in combination with an invert emulsion base, thinners, emulsifiers and weighting agents. (Burrows Tr. at p. 61 l. 3 to p. 62 l. 5.)

- **35 U.S.C. § 102(e) – prior patent publication filed by different invention entity**

- (R)) International Application No. PCT/US00/35609 (International Publication No. WO 02/053675), entitled "Thinners for Invert Emulsions," which was filed on December 29, 2000 and published on July 11, 2002.
- (S) International Application No. PCT/US00/35610 (International Publication No. WO 02/053676), entitled "Thinners for Invert Emulsions," which was filed on December 29, 2000 and published on July 11, 2002.

(b) **Anticipation and/or Obviousness:**

- (A) Prior Art Item (A) anticipates claims 1, 2, 3, 5, 6, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 20, 21, 22, 33, 39, 42, 43, 45, 47, 48, 49, 50, 52, 53, 54, 55, 56, 58, 59, 60, 71, 77, 80, 81, 85, 86, 87, 88, 90, 92, 93, 94, 95, 96, 97, 108, 114, 117, 118, 121, 123, 124, 125, 126, 127, 129, 140, 146, and 149 of the '832 patent. Prior Art combinations (A)/(H); (A/L); (A/M); (A/N); and (A/O) each render obvious claim 1 of the '832 patent. Prior Art combination (A/Q) renders obvious claims 12, 13, 22, 39, 50, 52, 60, 77, 88, 90, 97, 114, 126, 129, 146. Prior Art combination (A)-

- (S) renders obvious claim 14. Prior Art combinations (A/I**) renders obvious claims 19, 20, 39, 57, 58, 77, 94, 95, 114, 125, 127, and 146. Prior Art combination (A/B/D-H/M-S) renders obvious claims 40, 78, 115, and 147. The motivation to combine these references comes expressly and/or implicitly from the prior art, from the knowledge of persons of ordinary skill, and/or from the nature of the problem to be solved.
- (B) Prior Art Item (B) anticipates claims 1*, 2, 8*, 9, 14, 17, 18, 19, 20, 22, 23, 39, 45, 47, 55, 56, 57, 58, 60, 61, 77, 85, 93, 94, 95, 97, 98, 114, 125, 126, 127, and 146. Prior Art combination (B/P) renders obvious claims 17, 19, 20, 55, 57, 58, 94, 95, 125, and 127. The motivation to combine these references comes expressly and/or implicitly from the prior art, from the knowledge of persons of ordinary skill, and/or from the nature of the problem to be solved.
- (C) Prior Art Item (D) anticipates claims 1, 39, 77, 114 and 146.
- (D) Prior Art Item (E) anticipates claims 1*, 6, 12, 39, 43, 50, 77, 81, 88, 114, 118 and 146.
- (E) Prior Art Item (F) anticipates claims 1*, 6, 39, 43, 77, 81, 114, 118, and 146.
- (F) Prior Art Item (G) anticipates claims 1, 6, 8, 14, 19, 39, 43, 77, 114, 81, 118, and 146.
- (G) Prior Art Item (H) anticipates claims 8, 39, 45, 77, 114, and 146.
- (H) Prior Art Item (I) anticipates claims 1, 8, 9, 17, 18, 42, 45, 47, 55, 56, 80, 85, 93, 117, and 121.
- (I) Prior Art Item (J) anticipates claims 1*, 6, 17, 43, 55, 81, and 118. Prior Art Item (J) renders obvious claims 21, 59, 96, and 149. The motivation to combine these references comes expressly and/or implicitly from the prior art, from the knowledge of persons of ordinary skill, and/or from the nature of the problem to be solved.
- (J) Prior Art Item (K) anticipates claims 1*, 6, 43, 81, and 118. Prior Art Item (K) renders obvious claims 20, 59, 95, and 125. The motivation to combine these references comes expressly and/or implicitly from the prior art, from the knowledge of persons of ordinary skill, and/or from the nature of the problem to be solved.
- (K) Prior Art Item (L) anticipates claims 8, 14, 17, 19, 21, 45, 55, 57, 59, 94, 96, 127, and 149.

** See Reference (I) at 195.

* See Reference (I) at 22.

- (L) Prior Art Item (M) anticipates claims 8, 14, 17, 19, 33, 39, 45, 55, 57, 71, 77, 94, 108, 114, 127, 140, and 146.
- (M) Prior Art Item (N) anticipates claims 8, 17, 20, 21, 22, 39, 45, 55, 58, 59, 77, 95, 96, 114, 125, 146, and 149.
- (N) Prior Art Item (O) anticipates claims 20, 22, 39, 58, 60, 77, 95, 97, 114, 125, 126, and 146.
- (O) Prior Art Item (P) anticipates claims 1, 6, 8, 18, 20, 22, 39, 43, 45, 56, 58, 60, 81, 93, 95, 97, 118, 125, and 126.
- (P) Prior Art Item (Q) anticipates claims 1, 6, 8, 9, 10, 11, 12, 16, 17, 18, 39, 42, 43, 45, 47, 48, 49, 50, 54, 55, 56, 77, 81, 85, 86, 87, 88, 93, 114, 118, 123, 124, and 146.
- (Q) Prior Art Item (R) anticipates claims 1*, 6, 12, 13, 17, 18, 20, 22, 39, 43, 50, 52, 55, 56, 58, 60, 77, 81, 88, 90, 93, 95, 97, 114, 118, 125, 126, 129, and 146.
- (R) Prior Art Item (S) anticipates claims 1*, 6, 12, 13, 39, 43, 50, 52, 77, 81, 88, 90, 114, 118, 129, and 146.

M-I reserves the right to assert additional combinations of Prior Art Items in addition to those outlined above.

(c) **Invalidity Claim Chart:**

See Claim Chart attached as Exhibit A. The lists of locations of each element in each reference are representative, and do not necessarily include each and every location.

M-I does not contend that any element of any claim asserted by Halliburton is governed by 35 U.S.C. § 112 ¶ 6.

(d) **35 U.S.C. § 112**

M-I contends that the following claims are not enabled and therefore are invalid:

- if the term “fragile gel drilling fluid” is an element of the claims, then all asserted claims are invalid based on indefiniteness under 35 U.S.C. § 112 ¶ 1, on the ground that, claims to a “**fragile gel drilling fluid**” are not enabled (Burrows Tr. pp. 37-43; 71-73; 103-105; 107-108; 219-221; and 225)
- if the term “fragile gel drilling fluid” is an element of the asserted claims, those claims are also invalid because the mechanism Halliburton uses to determine if a fluid is a “**fragile gel drilling fluid**,” a Brookfield test, is not disclosed, and is done using a modified instrument not available outside Halliburton. (Burrows Tr. p. 112)
- asserted claims 33, 71, 108, and 140 are invalid based on indefiniteness under 35 U.S.C. § 112 ¶ 1, on the ground that these claims to an “**ester-free**” drilling fluid are not enabled; and/or are invalid under 35 U.S.C. §§ 101, 112 ¶2 on the ground that these claims are not directed to applicants’ invention. (See Burrows Tr. at p. 85 l. 16 to p. 86 l. 24 (indicating that late 2003 was the first time that Halliburton did any work in trying to develop a fluid that had fragile gels or fragile gel properties that did not include esters in the emulsion base); Huffman Tr. at p. 90)
- asserted claims 42, 80, 117, 121 are invalid based on indefiniteness under 35 U.S.C. § 112 ¶ 1, on the ground that these claims to “**instantaneously**” are not described or enabled. (Burrows Tr. at p. 71-73)
- asserted claims 9-10, 47-48, 85-86, and 123 are invalid based on indefiniteness under 35 U.S.C. § 112 ¶ 1, on the ground that these claims to “**immediately**” are not described or enabled. (Burrows Tr. at p. 72-73)

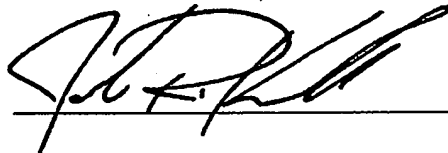
- asserted claims 11, 49, 87, and 128 are invalid based on indefiniteness under 35 U.S.C. § 112 ¶ 1, on the ground that these claims to **“no appreciable pressure spike”** are not described or enabled. (Burrows Tr. at p. 73, 78)
- asserted claims 24, 62, 99, and 128 are invalid based on indefiniteness under 35 U.S.C. § 112 ¶ 1, on the ground that these claims to **“low difference in surface and downhole equivalent circulating densities”** are not described or enabled. (Burrows Tr. at p. 79-80)
- asserted claim 128 is invalid based on indefiniteness under 35 U.S.C. § 112 ¶ 1, on the ground that this claim to **“no significant sag”** is not described or enabled. (Burrows Tr. at p. 80)
- asserted claim 128 is invalid based on indefiniteness under 35 U.S.C. § 112 ¶ 1, on the ground that this claim to **“generally flat rheology”** is not described or enabled. (Burrows Tr. p. 80-82)
- asserted claims 40, 78, 115, 147 are invalid based on indefiniteness under 35 U.S.C. § 112 ¶ 1, on the ground that these claim to incorporating additives **“quickly”** are not described or enabled.

M-I contends that asserted method claims 1-3, 6, 8-24, 33, 39-40, 42-43, 45-62, 71, 77-78, 80-81, 83-99, 108, 114-115, and 117 are invalid based on indefiniteness under 35 U.S.C. § 112 ¶ 2 and, alternatively, are invalid as improper process claims under 35 U.S.C. § 101, on the ground that these claims recite mere “use” and fail to particularly point out and distinctly claim any active, positive steps of the method. M-I further contends that asserted claims 1-3, 6, 8-24, 33, 39-40, 42-43, 45-62, 71, 77-78, 80-81, 83-99, 108, 114-115, and 117 are invalid based on

indefiniteness under 35 U.S.C. § 112 ¶ 1 on the ground that these claims are not enabled method claims.

M-I reserves the right to supplement its Preliminary Invalidity Contentions under P.R. 3-3 should additional grounds of invalidity be discovered.

Respectfully submitted,



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CERTIFICATE OF SERVICE

I hereby certify that the following counsel of record are being served this 28th day of October, 2005, with a copy of M-I, L.L.C.'s PRELIMINARY INVALIDITY CONTENTIONS via United States First Class Mail.

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A handwritten signature in black ink, appearing to be "M. E. Jones", written over a horizontal line.

Asserted Claim 1

Element	References	Location of Element in Each Reference
1. A method for conducting a drilling operation in a subterranean formation using a fragile gel drilling fluid comprising:		SEE ENDNOTE 1
		Prior Art drilling fluids combining elements (a) through (d) below — invert emulsion base, thinners, emulsifiers, and weighting agents — commonly were used in drilling operations that included running casing in a borehole before June of 2001, one year before the filing date of the '832 patent. (I) at pp. 21-22, 29, 109-110.
(a) an invert emulsion base;	(A) (B) (D) (E) (F) (G) (J) (H) (K) (L) (M) (N) (O) (P) (Q) (R) (S)	p. 1 cols. 1-2; p. 2 cols. 1-2 Petrofree brochure pp. 1-2, 5 (table); RM-63 brochure pp. 1-2 col. 1 ll. 50-52; col. 6 ll. 12-19 abstract; col. 1 ll. 10-11, 34-40; col. 3 ll. 39-64; col. 8 ll. 15-63; col. 9 ll. 3-31 abstract; col. 1 ll. 37-49; col. 1 l. 62 to col. 2 l. 3; col. 3 ll. 38-50; col. 12 ll. 20-26; col. 14 ll. 63-68 pp. 1-2, 8-9 & table 1 p. 1 cols. 1-2; p. 3 col. 1; p. 4 col. 1 pp. 4-5, 13, 15-16 p. 363 col. 1; p. 364 col. 1; p. 368 col. 1 p. 1 cols. 1-2; p. 2 col. 2; p. 3 col. 1 p. 1 cols. 1-2; p. 2 col. 1; p. 4 col. 1; table 5 p. 1 cols. 1-2; p. 2 col. 2 p. 1 cols. 1-2; tables 9-10 pp. 2, 5, 7 HAL_0015055, 0015102; See Reference (A) above p. 1 ll. 7-8, 22-26; p. 5 ll. 6-18; p. 7 l. 29 to p. 8 l. 26; p. 11 l. 30 to p. 12 l. 2 (table); p. 15 ll. 15-19 abstract; p. 1 ll. 7, 21-25; p. 5 l. 24 to p. 6 l. 4; p. 9 l. 19 to p. 10 l. 17; p. 16 ll. 16-35 (table)
(b) one or more thinners;	(A) (B) (C) (D) (E) (F) (G) (H) (I)	p. 3 at cols. 1-2; Fig. 4; Figs. 13-14 col. 13 ll. 29-33; col. 15 ll. 5-6 Petrofree brochure p. 5 (table) col. 1 l. 28 to col. 2 l. 31 abstract; col. 2 ll. 52-50; col. 3 l. 7 to col. 4 l. 60; col. 5 ll. 48-57 p. 2 ll. 15, 26; p. 4 ll. 29-32; p. 9 table 1 p. 5 col. 1 p. 365 col. 1; p. 367 col. 1 pp. 195, 204

Element	References	Location of Element in Each Reference
	(J) (K) (P) (Q) (R) (S)	abstract; col. 3 ll. 47-49, 60-64; col. 4 ll. 18-30; col. 4 l. 58 to col. 5 l. 33; col. 6 ll. 19-29 pp. 18-19 p. 4 HAL_0015067, 0015202-03; See Reference (A) above p. 1 ll. 7-10; p. 2 ll. 14-17; p. 4 ll. 1-10; p. 5 l. 19 to p. 6 l. 4; p. 6 l. 8 to p. 7 l. 4; p. 12 ll. 1-2 (table), 7-16; p. 15 ll. 21-24 abstract; p. 1 ll. 8-9; p. 2 ll. 14-17; p. 3 l. 16 to p. 4 l. 19; p. 6 ll. 5-30; p. 13 ll. 19-30; p. 14 ll. 3-31; p. 16 (table); p. 17 ll. 5-11
(c) one or more emulsifiers; and	(A) (B) (D) (E) (F) (G) (H) (J) (K) (L) (M) (N) (O) (P) (Q) (R) (S)	p. 1 cols. 1-2; p. 2 cols. 1-2 Petrofree brochure pp. 1, 5 (table) col. 6 ll. 12-19 abstract; col. 1 ll. 40-42; col. 3 ll. 43-46, 52-54; col. 9 ll. 50-63; col. 10 ll. 21-28 col. 2 ll. 1-4; col. 12 l. 60; col. 15 ll. 7-10 p. 1 col. 2; p. 3 col. 1 p. 365 col. 2; p. 366 col. 2 p. 1 l. 34; p. 2 ll. 11-12, 22-23; p. 7 ll. 22-35; p. 9 l. 3 & table 1 abstract; pp. 4-9 p. 3 col. 1 p. 3 cols. 1-2; p. 4 col. 1; p. 5 col. 1; figs. 3-4 p. 1 cols. 1-2; p. 2 cols. 1-2; p. 5 col. 1 p. 2 col. 1; tables 9-10 pp. 4, 7 HAL_0015055; See Reference (A) above p. 1 ll. 27-29; p. 10 ll. 31-33; p. 12 ll. 1-2 (table) p. 1 ll. 26-28; p. 12 ll. 29-31; p. 16 (table)
(d) one or more weighting agents,	(A) (B) (D) (E) (F) (G) (H) (J) (K) (L) (M) (N)	p. 1 col. 1; p. 2 col. 1 Petrofree brochure p. 5 (table); RM-63 brochure pp. 1-2 col. 6 ll. 12-19 abstract; col. 1 ll. 40-42; col. 3 ll. 43-46, 52-54; col. 10 ll. 8-15 col. 2 ll. 1-5; col. 13 ll. 9-12; col. 15 l. 11 p. 5 col. 2; p. 3 col. 1; p. 4 col. 2 p. 367 col. 2 p. 1 l. 35; p. 2 ll. 12, 23; p. 4 ll. 16-18; p. 8 ll. 1-3; p. 9 l. 8 & table 1 pp. 18, 21 p. 1 col. 2; p. 3 col. 1; p. 4 col. 1; p. 6 col. 1 fig. 9 & p. 4 cols. 1-2; fig. 15 & p. 5 col. 2; p. 6 col. 2 p. 1 cols. 1-2; p. 2 cols. 1-2; p. 4 col. 1 to p. 5 col. 1

Element	References	Location of Element in Each Reference
	(O) (P) (Q)	p. 1 col. 1; p. 2 col. 1; tables 9-10 pp. 4, 7 HAL_0015055; See Reference (A) above
	(R) (S)	p. 1 ll. 27-29; p. 2 ll. 10-11; p. 10 ll. 23-30; p. 12 ll. 1-2 (table) p. 1 ll. 26-28; p. 2 ll. 10-11; p. 12 ll. 20-28; p. 16 (table)

Element	References	Location of Element in Each Reference
wherein said operation includes running casing in a borehole.	(A) (D) (G) (H) (L) (M) (N) (O) (P) (Q)	p. 3 col. 1; Figs. 13-14 col. 1 ll. 16-22; col. 4 l. 61 to col. 5 l. 1; col. 6 ll. 16-26 Figs. 2-3 p. 367 col. 1 p. 3 col. 2; p. 6 col. 1 p. 5 cols. 1-2; p. 6 cols. 1-2 p. 2 col. 2 Fig. 1 pp. 1, 6 HAL_0015056; See Reference (A) above

Asserted Claim 6
(depends from Asserted Claim 1)

Element	References	Location of Element in Each Reference
6. The method of claim 1 wherein said invert emulsion has a continuous base comprised of at least one component selected from at least one of the following groups: (i) esters prepared from fatty acids and alcohols, esters prepared from olefins and fatty acids or alcohols; (ii) olefins comprising linear alpha olefins, isomerized olefins having a straight chain, olefins having a branched structure, isomerized olefins having a cyclic structure, olefin hydrocarbons; (iii) paraffin hydrocarbons comprising linear paraffins, branched paraffins, poly-branched paraffins, cyclic paraffins, isoparaffins; (iv) mineral oil hydrocarbons; (v) glyceride triesters comprising rapeseed oil, olive oil, canola oil, castor oil, coconut oil, corn oil, cottonseed oil, lard oil, linseed oil, neatsfoot oil, palm oil, peanut oil, perilla oil, rice bran oil, safflower oil, sardine oil, sesame oil, soybean oil, sunflower oil; and (vi) naphthenic hydrocarbons.	(A) (E) (F) (G) (J) (K) (P) (Q) (R) (S)	p. 1 cols. 1-2; p. 3 col. 1; tables 2-5; Fig. 16 col. 2 ll. 1-15 col. 1 ll. 41-49; col. 2 ll. 26-29, 36-46; col. 7 ll. 1-6, 39-48 p. 1 col. 2 p. 2 ll. 1, 3-4, 13-14, 25, 30; p. 3 ll. 8-9, 15-31; p. 4 ll. 1-15; p. 8 ll. 30-35; p. 9 table 1 pp. 13, 15-16 p. 2 HAL_0015053-54; See Reference (A) above p. 8 ll. 6-26; p. 9 ll. 5-22; p. 15 ll. 15-24 p. 9 l. 29 to p. 10 l. 17; p. 10 l. 29 to p. 11 l. 15

Asserted Claim 8
(depends from Asserted Claim 1)

Element	References	Location of Element in Each Reference
8. The method of claim 1 wherein said fragile gel drilling fluid is also used in drilling said borehole.	(A) (G) (H) (M) (N) (P) (Q)	p. 1 col. 2; p. 3 col. 1; Figs. 13-14 p. 4 col. 1 pp. 367-68 p. 1 p. 1 p. 1 HAL 0015055; See Reference (A) above

Asserted Claim 9
(depends from Asserted Claims 1 and 8)

Element	References	Location of Element in Each Reference
9. The method of claim 8 wherein said fragile gel is a structure capable of suspending drill cuttings at rest and that may be immediately disrupted by movement of said fluid.	(A) (B) (I) (Q)	p. 2 cols. 1-2; p. 3 col. 1 RM-63 brochure pp. 1-2 p. 39 ll. 3-7 See Reference (A) above

Asserted Claim 10
(depends from Asserted Claims 1 and 8)

Element	References	Location of Element in Each Reference
10. The method of claim 8 wherein said fragile gel reverts to a flowable or liquid state immediately upon resumption of drilling after a period of rest.	(A) (Q)	p. 2 cols. 1-2; p. 3 col. 1 See Reference (A) above

Asserted Claim 11
(depends from Asserted Claims 1 and 8)

Element	References	Location of Element in Each Reference
11. The method of claim 8 wherein no appreciable pressure spike is observed by pressure-while-drilling equipment when said drilling is resumed.	(A) (L) (Q)	p. 2 col. 2 to p. 3 col. 1; p. 3 col. 1 & Figs. 11-12 p. 5 col. 2 See Reference (A) above

Asserted Claim 16
(depends from Asserted Claims 1 and 8)

Element	References	Location of Element in Each Reference
16. The method of claim 8 wherein the ECDs are less than about 0.5.	(A) (Q)	Figs. 11-12; p. 3 col. 1; p. 4 col. 1 See Reference (A) above

Asserted Claim 15
(depends from Asserted Claims 1 and 8)

Element	References	Location of Element in Each Reference
16. The method of claim 8 wherein the equivalent circulating density of said drilling fluid approximates the surface density of said drilling fluid.	(A)	p. 3 col. 1; p. 4 col. 1; Figs. 11-12
	(G)	p. 1 col. 1; p. 2 col. 1; p. 6
	(L)	p. 1 col. 2; p. 3 col. 2
	(N)	p. 1 col. 2; p. 6 col. 1
	(Q)	See Reference (A) above

Asserted Claim 17
(depends from Asserted Claims 1 and 8)

Element	References	Location of Element in Each Reference
17. The method of claim 8 wherein said drilling is in deep water.	(A) (H) (I) (L) (M) (N) (Q) (R)	title; p. 1 col. 1; p. 2 cols. 1-2 p. 366 col. 1; p. 367 col. 1 p. 29 ll. 8-16 p. 1 col. 2; p. 2 col. 2; p. 6 col. 1 p. 1 cols. 1-2 p. 1 col. 2; p. 3 col. 1 HAL_0015053; See Reference (A) above p. 2 l. 30 to p. 3 l. 9; p. 3 ll. 24-33; p. 5 ll. 8-12

Asserted Claim 18
(depends from Asserted Claims 1 and 8)

Element	References	Location of Element in Each Reference
18. The method of claim 8 wherein said drilling fluid is tolerant to contaminants, wherein said contaminants comprise drill cuttings from said drilling.	(A) (I) (L) (O) (P) (Q) (R)	p. 1 cols. 1-2, p. 2 cols. 1-2; Figs. 4-6 p. 30 l. 3 to p. 31 l. 8 p. 1 col. 2 p. 1 col. 1; p. 3 col. 1 p. 1 HAL_0015055; See Reference (A) above p. 13 ll. 1-5; p. 14 (table 1); pp. 16-19 (tables 2, 4, 6, 9)

Asserted Claim 21
(depends from Asserted Claims 1 and 8)

Element	References	Location of Element in Each Reference
21. The method of claim 8 wherein said drilling is conducted without significant loss of drilling fluid.	(I) (L) (N)	p. 2 ll. 23-24; p. 8 ll. 7-10 p. 3 at col. 2 ll. 23-26 p. 5 at col. 2 ll. 7-29

Asserted Claim 22
(depends from Asserted Claims 1 and 8)

Element	References	Location of Element in Each Reference
22. The method of claim 8 wherein said drilling fluid does not require organophilic clays to provide filtration control.	(B) (N) (O) (Q) (R)	Petrofree brochure p. 6; RM-63 brochure p. 1 p. 2 col. 2; p. 5 col. 2 p. 2 cols. 1-2; p. 3 col. 1; p. 9 HAL 0015053-55; See Reference (A) above p. 11 ll. 12-14

Asserted Claim 23
(depends from Asserted Claims 1 and 8)

Element	References	Location of Element in Each Reference
23. The method of claim 8 wherein said drilling fluid demonstrates lower differences in surface and downhole equivalent circulating densities at faster drilling rates.	(B)	p. 3, 7

Asserted Claim 12

(depends from Asserted Claim 1)

Element	References	Location of Element in Each Reference
12. The method of claim 1 wherein said thinner reduces the viscosity of said drilling fluid at lower temperatures to a greater extent than it reduces the viscosity of said drilling fluid at higher temperatures.	(E) (Q) (R) (S)	col. 4 ll. 24-30 HAL_0015054; HAL_0015101-102 p. 3 ll. 24-33; p. 7 ll. 17-25; p. 14 (table 1a); p. 16 (tables 2-3); p. 17 (tables 4-5); p. 18 (table 7); p. 19 (table 8) p. 18 (table 1); p. 20 (table 3); p. 21 (table 5); p. 22 (tables 6-7); p. 23 (table 9); p. 24 (table 10); p. 25 (tables 12-13); p. 26 (tables 14-15)

Asserted Claim 13
(depends from Asserted Claim 1)

Element	References	Location of Element in Each Reference
13. The method of claim 1 wherein said drilling fluid has a lower yield point at lower temperatures than at higher temperatures.	(R) (S)	p. 7 ll. 17-23; p. 17 (table 5) p. 18 (table 1)

Asserted Claim 14
(depends from Asserted Claim 1)

Element	References	Location of Element in Each Reference
14. The method of claim 1 wherein said drilling fluid is visco-elastic.	(G)	p. 1 col. 1; p. 3 col. 2
	(L)	p. 1 col. 2; p. 3 col. 1
	(M)	p. 1 col. 1; p. 3 col. 2 to p. 4 col. 1

Asserted Claim 19
(depends from Asserted Claim 1)

Element	References	Location of Element in Each Reference
19. The method of claim 1 whercin said fluid does not exhibit sag when at rest.	(B) (G) (L) (M)	RM-63 brochure p. 1 p. 4 col. 1 p. 1 col. 2; p. 3 col. 2; p. 6 cols. 1-2 p. 1 col. 1; p. 4 cols. 1-2; p. 5 col. 2; p. 6 cols. 1-2

Asserted Claim 20
(depends from Asserted Claim 1)

Element	References	Location of Element in Each Reference
20. The method of claim 1 wherein said drilling fluid is substantially free of organophilic clay.	(B) (N) (O) (Q) (R)	Petrofree brochure p. 6; RM-63 brochure p. 1 p. 2 col. 2; p. 5 col. 2 p. 2 cols. 1-2; p. 3 col. 1; p. 9 HAL_0015053-55; See Reference (A) above p. 11 ll. 12-14

Asserted Claim 33
(depends from Asserted Claim 1)

Element	References	Location of Element in Each Reference
33. The method of claim 1 wherein said drilling fluid is ester-free.	(A)	Figs. 15-16; p. 1 col. 2; p. 2 col. 2
	(H)	pp. 3-6
	(M)	p. 1 col. 2 to p. 2 col. 1
	(N)	p. 2 col. 2 to p. 3, col. 1, pp. 8-12

Asserted Claim 39
(depends from Asserted Claim 1)

Element	References	Location of Element in Each Reference
39. The method of claim 1 wherein said drilling fluid comprises at least one additive selected from the group consisting of rheology control agents, viscosifiers, filtration control agents, and HTHP additives.	(A)	p. 1; See Reference (I) at 195
	(B)	Petrofree brochure p. 5 (table); RM-63 brochure p. 1
	(D)	col. 6 ll. 12-16
	(E)	col. 2 ll. 40-45; col. 3 ll. 42-46, 52-55
	(F)	col. 2 ll. 1-6; col. 12 ll. 60-62; col. 13 ll. 13-16
	(G)	p. 1 col. 2 to p. 2 col. 1
	(H)	p. 365 col. 1; p. 367 col. 1
	(M)	p. 3 col. 2; p. 4 col. 1
	(N)	p. 2 col. 2; p. 5 col. 2
	(O)	p. 1 col. 1; tables 9-10
	(P)	p. 4
	(Q)	HAL_0015055
	(R)	p. 1 ll. 27-30; p. 10 ll. 31-33
	(S)	p. 1 ll. 26-29; p. 12 ll. 29-31

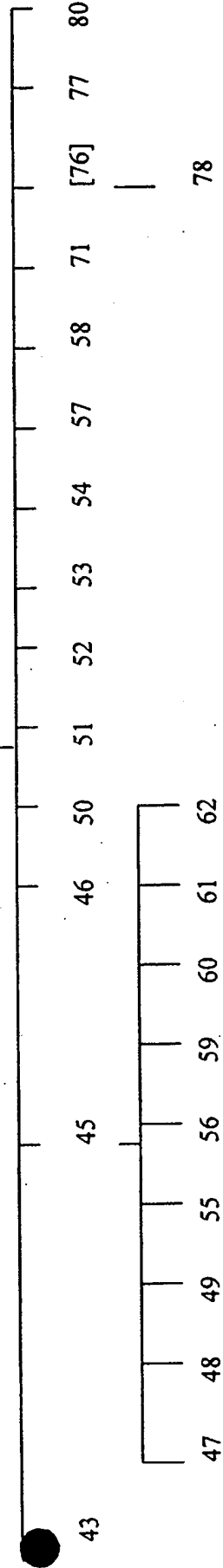
Asserted Claim 42

(depends from Asserted Claim 1)

Element	References	Location of Element in Each Reference
42. The method of claim 1 wherein said drilling fluid forms a structure that is capable of suspending drill cuttings at rest and that is instantaneously disruptible by movement.	(A) (I) (Q)	p. 2 cols. 1-2; p. 2 col. 2 to p. 3 col. 1 p. 39 ll. 3-7 See Reference (A) above

Asserted Claim 2
& Dependent Asserted Claims

2



Asserted Claim 2

Element	References	Location of Element in Each Reference
2. A method for conducting a drilling operation in a subterranean formation using a fragile gel drilling fluid comprising:		SEE <i>ENDNOTE</i>
Drilling fluids combining elements (a) through (d) below — invert emulsion base, thinners, emulsifiers, and weighting agents — commonly were used in drilling operations that included running casing in a borehole before June of 2001, one year before the filing date of the '832 patent. (I) at pp. 21-22, 29, 109-110.		
(a) an invert emulsion base;	(A) (B) (D) (E) (F) (G) (J) (H) (K) (L) (M) (N) (O) (P) (Q) (R) (S)	p. 1 cols. 1-2; p. 2 cols. 1-2 Petrofree brochure pp. 1-2, 5 (table); RM-63 brochure pp. 1-2 col. 1 ll. 50-52; col. 6 ll. 12-19 abstract; col. 1 ll. 10-11, 34-40; col. 3 ll. 39-64; col. 8 ll. 15-63; col. 9 ll. 3-31 abstract; col. 1 ll. 37-49; col. 1 l. 62 to col. 2 l. 3; col. 3 ll. 38-50; col. 12 ll. 20-26; col. 14 ll. 63-68 pp. 1-2, 8-9 & table 1 p. 1 cols. 1-2; p. 3 col. 1; p. 4 col. 1 pp. 4-5, 13, 15-16 p. 363 col. 1; p. 364 col. 1; p. 368 col. 1 p. 1 cols. 1-2; p. 2 col. 2; p. 3 col. 1 p. 1 cols. 1-2; p. 2 col. 1; p. 4 col. L; table 5 p. 1 cols. 1-2; p. 2 col. 2 p. 1 cols. 1-2; tables 9-10 pp. 2, 5, 7 HAL_0015055, 0015102; See Reference (A) above p. 1 ll. 7-8, 22-26; p. 5 ll. 6-18; p. 7 l. 29 to p. 8 l. 26; p. 11 l. 30 to p. 12 l. 2 (table); p. 15 ll. 15-19 abstract; p. 1 ll. 7, 21-25; p. 5 l. 24 to p. 6 l. 4; p. 9 l. 19 to p. 10 l. 17; p. 16 ll. 16-35 (table)
(b) one or more thinners;	(A) (B) (C) (D) (E) (F) (G) (H) (I) (J)	p. 3 at cols. 1-2; Fig. 4; Figs. 13-14 col. 13 ll. 29-33; col. 15 ll. 5-6 Petrofree brochure p. 5 (table) col. 1 l. 28 to col. 2 l. 31 abstract; col. 2 ll. 52-50; col. 3 l. 7 to col. 4 l. 60; col. 5 ll. 48-57 p. 2 ll. 15, 26; p. 4 ll. 29-32; p. 9 table 1 p. 5 col. 1 p. 365 col. 1; p. 367 col. 1 pp. 195, 204 abstract; col. 3 ll. 47-49, 60-64; col. 4 ll. 18-30; col. 4 l. 58 to col. 5 l. 33; col. 6 ll. 19-29

Element	References	Location of Element in Each Reference
	(K) (P) (Q) (R) (S)	pp. 18-19 p. 4 HAL_0015067, 0015202-03; See Reference (A) above p. 1 ll. 7-10; p. 2 ll. 14-17; p. 4 ll. 1-10; p. 5 l. 19 to p. 6 l. 4; p. 6 l. 8 to p. 7 l. 4; p. 12 ll. 1-2 (table), 7-16; p. 15 ll. 21-24 abstract; p. 1 ll. 8-9; p. 2 ll. 14-17; p. 3 l. 16 to p. 4 l. 19; p. 6 ll. 5-30; p. 13 ll. 19-30; p. 14 ll. 3-31; p. 16 (table); p. 17 ll. 5-11
(c) one or more emulsifiers; and	(A) (B) (D) (E) (F) (G) (H) (I) (K) (L) (M) (N) (O) (P) (Q) (R) (S)	p. 1 cols. 1-2; p. 2 cols. 1-2 Petrofree brochure pp. 1, 5 (table) col. 6 ll. 12-19 abstract; col. 1 ll. 40-42; col. 3 ll. 43-46, 52-54; col. 9 ll. 50-63; col. 10 ll. 21-28 col. 2 ll. 1-4; col. 12 l. 60; col. 15 ll. 7-10 p. 1 col. 2; p. 3 col. 1 p. 365 col. 2; p. 366 col. 2 p. 1 l. 34; p. 2 ll. 11-12, 22-23; p. 7 ll. 22-35; p. 9 l. 3 & table 1 abstract; pp. 4-9 p. 3 col. 1 p. 3 cols. 1-2; p. 4 col. 1; p. 5 col. 1; figs. 3-4 p. 1 cols. 1-2; p. 2 cols. 1-2; p. 5 col. 1 p. 2 col. 1; tables 9-10 pp. 4, 7 HAL_0015055; See Reference (A) above p. 1 ll. 27-29; p. 10 ll. 31-33; p. 12 ll. 1-2 (table) p. 1 ll. 26-28; p. 12 ll. 29-31; p. 16 (table)
(d) one or more weighting agents,	(A) (B) (D) (E) (F) (G) (H) (J) (K) (L) (M) (N) (O) (P)	p. 1 col. 1; p. 2 col. 1 Petrofree brochure p. 5 (table); RM-63 brochure pp. 1-2 col. 6 ll. 12-19 abstract; col. 1 ll. 40-42; col. 3 ll. 43-46, 52-54; col. 10 ll. 8-15 col. 2 ll. 1-5; col. 13 ll. 9-12; col. 15 l. 11 p. 5 col. 2; p. 3 col. 1; p. 4 col. 2 p. 367 col. 2 p. 1 l. 35; p. 2 ll. 12, 23; p. 4 ll. 16-18; p. 8 ll. 1-3; p. 9 l. 8 & table 1 pp. 18, 21 p. 1 col. 2; p. 3 col. 1; p. 4 col. 1; p. 6 col. 1 fig. 9 & p. 4 cols. 1-2; fig. 15 & p. 5 col. 2; p. 6 col. 2 p. 1 cols. 1-2; p. 2 cols. 1-2; p. 4 col. 1 to p. 5 col. 1 p. 1 col. 1; p. 2 col. 1; tables 9-10 pp. 4, 7

Element	References	Location of Element in Each Reference
	(Q) (R) (S)	HAL 0015055; See Reference (A) above p. 1 ll. 27-29; p. 2 ll. 10-11; p. 10 ll. 23-30; p. 12 ll. 1-2 (table) p. 1 ll. 26-28; p. 2 ll. 10-11; p. 12 ll. 20-28; p. 16 (table)
wherein said drilling fluid is visco-elastic.	(G) (L) (M)	p. 1 col. 1; p. 3 col. 2 p. 1 col. 2; p. 3 col. 1 p. 1 col. 1; p. 3 col. 2 to p. 4 col. 1

Asserted Claim 43
(depends from Asserted Claim 2)

Element	References	Location of Element in Each Reference
<p>43. The method of claim 2 wherein said invert emulsion has a continuous base comprised of at least one component selected from at least one of the following groups:</p> <p>(i) esters prepared from fatty acids and alcohols, esters prepared from olefins and fatty acids or alcohols;</p> <p>(ii) olefins comprising linear alcohols, isomerized olefins having a straight chain, olefins having a branched structure, isomerized olefins having a cyclic structure; olefin hydrocarbons;</p> <p>(iii) paraffin hydrocarbons comprising linear paraffins, branched paraffins, poly-branched paraffins, cyclic paraffins, isoparaffins;</p> <p>(iv) mineral oil hydrocarbons;</p> <p>(v) glyceride triesters comprising rapeseed oil, olive oil, canola oil, castor oil, coconut oil, corn oil, cottonseed oil, lard oil, linseed oil, neatsfoot oil, palm oil, peanut oil, perilla oil, rice bran oil, safflower oil, sardine oil, sesame oil, soybean oil, sunflower oil; and</p> <p>(vi) naphthenic hydrocarbons.</p>	<p>(A) (E) (F) (G) (J) (K) (P) (Q) (R) (S)</p>	<p>p. 1 cols. 1-2; p. 3 col. 1; tables 2-5; Fig. 16 col. 2 ll. 1-15 col. 1 ll. 41-49; col. 2 ll. 26-29, 36-46; col. 7 ll. 1-6, 39-48 p. 1 col. 2 p. 2 ll. 1, 3-4, 13-14, 25, 30; p. 3 ll. 8-9, 15-31; p. 4 ll. 1-15; p. 8 ll. 30-35; p. 9 table 1 pp. 13, 15-16 p. 2 HAL. 0015053-54; See Reference (A) above p. 8 ll. 6-26; p. 9 ll. 5-22; p. 15 ll. 15-24 p. 9 l. 29 to p. 10 l. 17; p. 10 l. 29 to p. 11 l. 15</p>

Asserted Claim 45
(depends from Asserted Claim 2)

Element	References	Location of Element in Each Reference
45. The method of claim 2 said operation includes drilling a borehole.	(A) (G) (H) (M) (N) (P) (Q)	p. 1 col. 2; p. 3 col. 1; Figs. 13-14 p. 4 col. 1 pp. 367-68 p. 1 p. 1 p. 1 HAL 0015055; See Reference (A) above

Asserted Claim 47
(depends from Asserted Claims 2 and 45)

Element	References	Location of Element in Each Reference
47. The method of claim 45 wherein said fragile gel is a structure capable of suspending drill cuttings that may be immediately disrupted by movement of said fluid.	(A) (B) (I) (Q)	p. 2 cols. 1-2; p. 3 col. 1 RM-63 brochure pp. 1-2 p. 39 ll. 3-7 See Reference (A) above

Asserted Claim 48
(depends from Asserted Claims 2 and 45)

Element	References	Location of Element in Each Reference
48. The method of claim 45 wherein said fragile gel reverts to a flowable or liquid state immediately upon resumption of drilling after a period of rest.	(A) (Q)	p. 2 cols. 1-2; p. 3 col. 1 See Reference (A) above

Asserted Claim 49
(depends from Asserted Claims 2 and 45)

Element	References	Location of Element in Each Reference
49. The method of claim 45 wherein no appreciable pressure spike is observed by pressure-while-drilling equipment when said drilling is resumed.	(A) (L) (Q)	p. 2 col. 2 to p. 3 col. 1; p. 3 col. 1 & Figs. 11-12 p. 5 col. 2 See Reference (A) above

Asserted Claim 55
(depends from Asserted Claims 2 and 45)

Element	References	Location of Element in Each Reference
55. The method of claim 45 wherein said drilling is in deep water.	(A)	title; p. 1 col. 1; p. 2 cols. 1-2
	(H)	p. 366 col. 1; p. 367 col. 1
	(I)	p. 29 ll. 8-16
	(L)	p. 1 col. 2; p. 2 col. 2; p. 6 col. 1
	(M)	p. 1 cols. 1-2
	(N)	p. 1 col. 2; p. 3 col. 1
	(Q)	HAL_0015053; See Reference (A) above
	(R)	p. 2 l. 30 to p. 3 l. 9; p. 3 ll. 24-33; p. 5 ll. 8-12

Asserted Claim 56
(depends from Asserted Claims 2 and 45)

Element	References	Location of Element in Each Reference
56. The method of claim 45 wherein said fluid is tolerant to contaminants, wherein said contaminants comprise drill cuttings from said drilling.	(A) (I) (L) (O) (P) (Q) (R)	p. 1 cols. 1-2; p. 2 cols. 1-2; Figs. 4-6 p. 30 l. 3 to p. 31 l. 8 p. 1 col. 2 p. 1 col. 1; p. 3 col. 1 p. 1 HAL_0015055; See Reference (A) above p. 13 ll. 1-5; p. 14 (table 1); pp. 16-19 (tables 2, 4, 6, 9)

Asserted Claim 59
(depends from Asserted Claims 2 and 45)

Element	References	Location of Element in Each Reference
59. The method of claim 45 wherein said drilling is conducted without significant loss of drilling fluid.	(J) (L) (N)	p. 2 ll. 23-24; p. 8 ll. 7-10 p. 3 at col. 2 ll. 23-26 p. 5 at col. 2 ll. 7-29

Asserted Claim 60
(depends from Asserted Claims 2 and 45)

Element	References	Location of Element in Each Reference
60. The method of claim 45 wherein said drilling fluid does not require organophilic clays to provide filtration control.	(B) (N) (O) (Q) (R)	Petrofree brochure p. 6; RM-63 brochure p. 1 p. 2 col. 2; p. 5 col. 2 p. 2 cols. 1-2; p. 3 col. 1; p. 9 HAL_0015053-55; See Reference (A) above p. 11 ll. 12-14

Asserted Claim 61
(depends from Asserted Claims 2 and 45)

Element	References	Location of Element in Each Reference
61. The method of claim 45 wherein said drilling fluid demonstrates lower differences in surface and downhole equivalent circulating densities at faster drilling rates.	(B)	p. 3, 7

Asserted Claim 46
(depends from Asserted Claim 2)

Element	References	Location of Element in Each Reference
46. The method of claim 2 wherein said operation includes cementing a borehole.	(D)	col. 1 ll. 16-33; col. 2 ll. 1-12; col. 6 ll. 19-22
	(G)	p. 5 cols. 1-2
	(M)	p. 6 col. 2
	(N)	p. 2 col. 2

Asserted Claim 50
(depends from Asserted Claim 2)

Element	References	Location of Element in Each Reference
50. The method of claim 2 wherein said thinner reduces the viscosity of said drilling fluid at lower temperatures to a greater extent than it reduces the viscosity of said drilling fluid at higher temperatures.	(E) (Q) (R) (S)	col. 4 ll. 24-30 HAL_0015054; HAL_0015101-102 p. 3 ll. 24-33; p. 7 ll. 17-25; p. 14 (table 1a); p. 16 (tables 2-3); p. 17 (tables 4-5); p. 18 (table 7); p. 19 (table 8) p. 18 (table 1); p. 20 (table 3); p. 21 (table 5); p. 22 (tables 6-7); p. 23 (table 9); p. 24 (table 10); p. 25 (tables 12-13); p. 26 (tables 14-15)

Asserted Claim 51
(depends from Asserted Claim 2)

Element	References	Location of Element in Each Reference
51. The method of claim 2 wherein said drilling fluid maintains its viscosity at higher temperatures.	(A) (P) (R) (S)	Figs. 13-14 See Reference (A) above p. 3 ll. 31-33; p. 7 ll. 23-25; p. 14 (table 1a); pp. 16-19 (tables 2-9) pp. 18-23 (e.g. tables 1, 4-6)

Asserted Claim 52
(depends from Asserted Claim 2)

Element	References	Location of Element in Each Reference
52. The method of claim 2 wherein said drilling fluid has a lower yield point at lower temperatures than at higher temperatures.	(R) (S)	p. 7 ll. 17-25; p. 17 (table 5) p. 18 (table 1)

Asserted Claim 53
(depends from Asserted Claim 2)

Element	References	Location of Element in Each Reference
53. The method of claim 2 wherein the equivalent circulating density of said drilling fluid approximates the surface density of said drilling fluid.	(A) (L) (P)	p. 2 col. 2 to p. 3 col. 1; p. 3 col. 1 & Figs. 11-12 p. 5 col. 2 See Reference (A) above

Asserted Claim 54
(depends from Asserted Claim 2)

Element	References	Location of Element in Each Reference
54. The method of claim 2 wherein the ECDs are less than about 0.5.	(A) (Q)	Figs. 11-12; p. 3 col. 1; p. 4 col. 1 See Reference (A) above

Asserted Claim 57
(depends from Asserted Claim 2)

Element	References	Location of Element in Each Reference
57. The method of claim 2 wherein said fluid does not exhibit sag when at rest.	(B) (G) (L) (M)	RM-63 brochure p. 1 p. 4 col. 1 p. 1 col. 2; p. 3 col. 2; p. 6 cols. 1-2 p. 1 col. 1; p. 4 cols. 1-2; p. 5 col. 2; p. 6 cols. 1-2

Asserted Claim 58
(depends from Asserted Claim 2)

Element	References	Location of Element in Each Reference
58. The method of claim 2 wherein said drilling fluid is substantially free of organophilic clay.	(B) (N) (O) (Q) (R)	Petrofree brochure p. 6; RM-63 brochure p. 1 p. 2 col. 2; p. 5 col. 2 p. 2 cols. 1-2; p. 3 col. 1; p. 9 HAL_0015053-55; See Reference (A) above p. 11 ll. 12-14

Asserted Claim 71
(depends from Asserted Claim 2)

Element	References	Location of Element in Each Reference
71. The method of claim 2 wherein said drilling fluid is ester-free.	(A)	Figs. 15-16; p. 1 col. 2; p. 2 col. 2
	(H)	pp. 3-6
	(M)	p. 1 col. 2 to p. 2 col. 1
	(N)	p. 2 col. 2 to p. 3, col. 1, pp. 8-12

Asserted Claim 77
(depends from Asserted Claim 2)

Element	References	Location of Element in Each Reference
77. The method of claim 2 wherein said drilling fluid comprises at least one additive selected from the group consisting of rheology control agents, viscosifiers, filtration control agents, and HTHP additives.	(A)	p. 1; See Reference (I) at 195
	(B)	Petrofree brochure p. 5 (table); RM-63 brochure p. 1
	(D)	col. 6 ll. 12-16
	(E)	col. 2 ll. 40-45; col. 3 ll. 42-46, 52-55
	(F)	col. 2 ll. 1-6; col. 12 ll. 60-62; col. 13 ll. 13-16
	(G)	p. 1 col. 2 to p. 2 col. 1
	(H)	p. 365 col. 1; p. 367 col. 1
	(M)	p. 3 col. 2; p. 4 col. 1
	(N)	p. 2 col. 2; p. 5 col. 2
	(O)	p. 1 col. 1; tables 9-10
	(P)	p. 4
	(Q)	HAL_0015055
	(R)	p. 1 ll. 27-30; p. 10 ll. 31-33
	(S)	p. 1 ll. 26-29; p. 12 ll. 29-31

Asserted Claim 80
(depends from Asserted Claim 2)

Element	References	Location of Element in Each Reference
80. The method of claim 2 wherein said drilling fluid forms a structure that is capable of suspending drill cuttings at rest and that is instantaneously disruptible by movement.	(A) (I) (Q)	p. 2 cols. 1-2; p. 2 col. 2 to p. 3 col. 1 p. 39 ll. 3-7 See Reference (A) above

Asserted Claim 3



Asserted Claim 3

Element	References	Location of Element in Each Reference
3. A method for drilling a borehole in a subterranean formation using a fragile gel drilling fluid comprising:		SEE ENDNOTE 1
		Prior Art drilling fluids combining elements (a) through (d) below — invert emulsion base, thinners, emulsifiers, and weighting agents — commonly were used in drilling operations that included running casing in a borehole before June of 2001, one year before the filing date of the '832 patent. (I) at pp. 21-22, 29, 109-110.
(a) an invert emulsion base;	(A) (B) (C) (D) (E) (F) (G) (H) (I) (J) (K) (L) (M) (N) (O) (P) (Q) (R) (S)	p. 1 cols. 1-2; p. 2 cols. 1-2 Petrofree brochure pp. 1-2, 5 (table); RM-63 brochure pp. 1-2 col. 1 ll. 50-52; col. 6 ll. 12-19 abstract; col. 1 ll. 10-11, 34-40; col. 3 ll. 39-64; col. 8 ll. 15-63; col. 9 ll. 3-31 abstract; col. 1 ll. 37-49; col. 1 l. 62 to col. 2 l. 3; col. 3 ll. 38-50; col. 12 ll. 20-26; col. 14 ll. 63-68 pp. 1-2, 8-9 & table 1 p. 1 cols. 1-2; p. 3 col. 1; p. 4 col. 1 pp. 4-5, 13, 15-16 p. 363 col. 1; p. 364 col. 1; p. 368 col. 1 p. 1 cols. 1-2; p. 2 col. 2; p. 3 col. 1 p. 1 cols. 1-2; p. 2 col. 1; p. 4 col. L; table 5 p. 1 cols. 1-2; p. 2 col. 2 p. 1 cols. 1-2; tables 9-10 pp. 2, 5, 7 HAL_0015055, 0015102; See Reference (A) above p. 1 ll. 7-8, 22-26; p. 5 ll. 6-18; p. 7 l. 29 to p. 8 l. 26; p. 11 l. 30 to p. 12 l. 2 (table); p. 15 ll. 15-19 abstract; p. 1 ll. 7, 21-25; p. 5 l. 24 to p. 6 l. 4; p. 9 l. 19 to p. 10 l. 17; p. 16 ll. 16-35 (table)
(b) one or more thinners;	(A) (B) (C) (D) (E) (F) (G) (H) (I) (J)	p. 3 at cols. 1-2; Fig. 4; Figs. 13-14 col. 13 ll. 29-33; col. 15 ll. 5-6 Petrofree brochure p. 5 (table) col. 1 l. 28 to col. 2 l. 31 abstract; col. 2 ll. 52-50; col. 3 l. 7 to col. 4 l. 60; col. 5 ll. 48-57 p. 2 ll. 15, 26; p. 4 ll. 29-32; p. 9 table 1 p. 5 col. 1 p. 365 col. 1; p. 367 col. 1 pp. 195, 204 abstract; col. 3 ll. 47-49, 60-64; col. 4 ll. 18-30; col. 4 l. 58 to col. 5 l. 33; col. 6 ll. 19-29

Element	References	Location of Element in Each Reference
	(K) (P) (Q) (R) (S)	pp. 18-19 p. 4 HAL_0015067, 0015202-03; See Reference (A) above p. 1 ll. 7-10; p. 2 ll. 14-17; p. 4 ll. 1-10; p. 5 l. 19 to p. 6 l. 4; p. 6 l. 8 to p. 7 l. 4; p. 12 ll. 1-2 (table), 7-16; p. 15 ll. 21-24 abstract; p. 1 ll. 8-9; p. 2 ll. 14-17; p. 3 l. 16 to p. 4 l. 19; p. 6 ll. 5-30; p. 13 ll. 19-30; p. 14 ll. 3-31; p. 16 (table); p. 17 ll. 5-11
(c) one or more emulsifiers; and	(A) (B) (D) (E) (F) (G) (H) (I) (J) (K) (L) (M) (N) (O) (P) (Q) (R) (S)	p. 1 cols. 1-2; p. 2 cols. 1-2 Petrofree brochure pp. 1, 5 (table) col. 6 ll. 12-19 abstract; col. 1 ll. 40-42; col. 3 ll. 43-46, 52-54; col. 9 ll. 50-63; col. 10 ll. 21-28 col. 2 ll. 1-4; col. 12 l. 60; col. 15 ll. 7-10 p. 1 col. 2; p. 3 col. 1 p. 365 col. 2; p. 366 col. 2 p. 1 l. 34; p. 2 ll. 11-12, 22-23; p. 7 ll. 22-35; p. 9 l. 3 & table 1 abstract; pp. 4-9 p. 3 col. 1 p. 3 cols. 1-2; p. 4 col. 1; p. 5 col. 1; figs. 3-4 p. 1 cols. 1-2; p. 2 cols. 1-2; p. 5 col. 1 p. 2 col. 1; tables 9-10 pp. 4, 7 HAL_0015055; See Reference (A) above p. 1 ll. 27-29; p. 10 ll. 31-33; p. 12 ll. 1-2 (table) p. 1 ll. 26-28; p. 12 ll. 29-31; p. 16 (table)
(d) one or more weighting agents,	(A) (B) (D) (E) (F) (G) (H) (I) (K) (L) (M) (N) (O) (P)	p. 1 col. 1; p. 2 col. 1 Petrofree brochure p. 5 (table); RM-63 brochure pp. 1-2 col. 6 ll. 12-19 abstract; col. 1 ll. 40-42; col. 3 ll. 43-46, 52-54; col. 10 ll. 8-15 col. 2 ll. 1-5; col. 13 ll. 9-12; col. 15 l. 11 p. 5 col. 2; p. 3 col. 1; p. 4 col. 2 p. 367 col. 2 p. 1 l. 35; p. 2 ll. 12, 23; p. 4 ll. 16-18; p. 8 ll. 1-3; p. 9 l. 8 & table 1 pp. 18, 21 p. 1 col. 2; p. 3 col. 1; p. 4 col. 1; p. 6 col. 1 fig. 9 & p. 4 cols. 1-2; fig. 15 & p. 5 col. 2; p. 6 col. 2 p. 1 cols. 1-2; p. 2 cols. 1-2; p. 4 col. 1 to p. 5 col. 1 p. 1 col. 1; p. 2 col. 1; tables 9-10 pp. 4, 7

Element	References	Location of Element in Each Reference
	(Q) (R) (S)	HAL_0015055; See Reference (A) above p. 1 ll. 27-29; p. 2 ll. 10-11; p. 10 ll. 23-30; p. 12 ll. 1-2 (table) p. 1 ll. 26-28; p. 2 ll. 10-11; p. 12 ll. 20-28; p. 16 (table)
wherein said drilling is in deep water and	(A) (H) (I) (L) (M) (N) (Q) (R)	title; p. 1 col. 1; p. 2 cols. 1-2 p. 366 col. 1; p. 367 col. 1 p. 29 ll. 8-16 p. 1 col. 2; p. 2 col. 2; p. 6 col. 1 p. 1 cols. 1-2 p. 1 col. 2; p. 3 col. 1 See Reference (A) above p. 2 l. 30 to p. 3 l. 9; p. 3 ll. 24-33; p. 5 ll. 8-12
the ECDs are less than about 0.5.	(A) (P)	Figs. 11-12; p. 3 col. 1; p. 4 col. 1 See Reference (A) above

Asserted Claim 81
(depends from Asserted Claim 3)

Element	References	Location of Element in Each Reference
<p>81. The method of claim 3 wherein said invert emulsion has a continuous base comprised of at least one component selected from at least one of the following groups:</p> <p>(i) esters prepared from fatty acids and alcohols, esters prepared from olefins and fatty acids or alcohols;</p> <p>(ii) olefins comprising linear alpha olefins, isomerized olefins having a straight chain, olefins having a branched structure, isomerized olefins having a cyclic structure; olefin hydrocarbons;</p> <p>(iii) paraffin hydrocarbons comprising linear paraffins, branched paraffins, poly-branched paraffins, cyclic paraffins, isoparaffins;</p> <p>(iv) mineral oil hydrocarbons;</p> <p>(v) glyceride triesters comprising rapeseed oil, olive oil, canola oil, castor oil, coconut oil, corn oil, cottonseed oil, lard oil, linseed oil, neatsfoot oil, palm oil, peanut oil, perilla oil, rice bran oil, safflower oil, sardine oil, sesame oil, soybean oil, sunflower oil; and</p> <p>(vi) naphthenic hydrocarbons.</p>	<p>(A) (E) (F) (G) (J) (K) (P) (Q) (R) (S)</p>	<p>p. 1 cols. 1-2; p. 3 col. 1; tables 2-5; Fig. 16 col. 2 ll. 1-15 col. 1 ll. 41-49; col. 2 ll. 26-29, 36-46; col. 7 ll. 1-6, 39-48 p. 1 col. 2 p. 2 ll. 1, 3-4, 13-14, 25, 30; p. 3 ll. 8-9, 15-31; p. 4 ll. 1-15; p. 8 ll. 30-35; p. 9 table 1 pp. 13, 15-16 p. 2 HAL_0015053-54; See Reference (A) above p. 8 ll. 6-26; p. 9 ll. 5-22; p. 15 ll. 15-24 p. 9 l. 29 to p. 10 l. 17; p. 10 l. 29 to p. 11 l. 15</p>

Asserted Claim 83
(depends from Asserted Claim 3)

Element	References	Location of Element in Each Reference
83. The method of claim 3 wherein said drilling fluid is further used in cementing said borehole.	(D) (G) (M) (N) (Q)	col. 1 ll. 16-33; col. 2 ll. 1-12; col. 6 ll. 19-22 p. 5 cols. 1-2 p. 6 col. 2 p. 2 col. 2 HAL_0015055

Asserted Claim 84
(depends from Asserted Claim 3)

Element	References	Location of Element in Each Reference
84. The method of claim 3 wherein said operation includes cementing a borehole.	(D)	col. 1 ll. 16-33; col. 2 ll. 1-12; col. 6 ll. 19-22
	(G)	p. 5 cols. 1-2
	(M)	p. 6 col. 2
	(N)	p. 2 col. 2

Asserted Claim 85
(depends from Asserted Claim 3)

Element	References	Location of Element in Each Reference
85. The method of claim 3 wherein said fragile gel is a structure capable of suspending drill cuttings that may be immediately disrupted by movement of said fluid.	(A) (B) (I) (Q)	p. 2 cols. 1-2; p. 3 col. 1 RM-63 brochure pp. 1-2 p. 39 ll. 3-7 See Reference (A) above

Asserted Claim 86
(depends from Asserted Claim 3)

Element	References	Location of Element in Each Reference
86. The method of claim 3 wherein said fragile gel reverts to a flowable or liquid state immediately upon resumption of drilling after a period of rest.	(A) (Q)	p. 2 cols. 1-2; p. 3 col. 1 See Reference (A) above

Asserted Claim 87
(depends from Asserted Claim 3)

Element	References	Location of Element in Each Reference
87. The method of claim 3 wherein no appreciable pressure spike is observed by pressure-while-drilling equipment when said drilling is resumed.	(A) (L) (Q)	p. 2 col. 2 to p. 3 col. 1; p. 3 col. 1 & Figs. 11-12 p. 5 col. 2 See Reference (A) above

Asserted Claim 88
(depends from Asserted Claim 3)

Element	References	Location of Element in Each Reference
88. The method of claim 3 wherein said thinner reduces the viscosity of said drilling fluid at lower temperatures to a greater extent than it reduces the viscosity of said drilling fluid at higher temperatures.	(E) (Q) (R) (S)	col. 4 ll. 24-30 HAL_0015054; HAL_0015101-102 p. 3 ll. 24-33; p. 7 ll. 17-25; p. 14 (table 1a); p. 16 (tables 2-3); p. 17 (tables 4-5); p. 18 (table 7); p. 19 (table 8) p. 18 (table 1); p. 20 (table 3); p. 21 (table 5); p. 22 (tables 6-7); p. 23 (table 9); p. 24 (table 10); p. 25 (tables 12-13); p. 26 (tables 14-15)

Asserted Claim 89
(depends from Asserted Claim 3)

Element	References	Location of Element in Each Reference
89. The method of claim 3 wherein said drilling fluid maintains its viscosity at higher temperatures.	(A) (P) (R) (S)	Figs. 13-14 See Reference (A) above p. 3 ll. 31-33; p. 7 ll. 23-25; p. 14 (table 1a); pp. 16-19 (tables 2-9) pp. 18-23 (e.g. tables 1, 4-6)

Asserted Claim 90
(depends from Asserted Claim 3)

Element	References	Location of Element in Each Reference
90. The method of claim 3 wherein said drilling fluid has a lower yield point at lower temperatures than at higher temperatures.	(R) (S)	p. 7 ll. 17-25; p. 17 (table 5) p. 18 (table 1)

Asserted Claim 91
(depends from Asserted Claims 3 and 90)

Element	References	Location of Element in Each Reference
91. The method of claim 90 wherein said higher temperatures are temperatures over about 120° F. and said lower temperatures range from about 40° F. to about 60° F.	(R) (S)	p. 2 ll. 19-28; p. 3 ll. 19-21; p. 7 ll. 19-25; p. 14 (table 1) & pp. 16-19 (tables 2-9) p. 2 l. 30 to p. 3 l. 3; p. 17 ll. 23-26; pp. 18-27 (tables 1-17)

Asserted Claim 92
(depends from Asserted Claim 3)

Element	References	Location of Element in Each Reference
92. The method of claim 3 wherein the equivalent circulating density of said drilling fluid approximates the surface density of said drilling fluid.	(A) (L) (P)	p. 2 col. 2 to p. 3 col. 1; p. 3 col. 1 & Figs. 11-12 p. 5 col. 2 See Reference (A) above

Asserted Claim 93
(depends from Asserted Claim 3)

Element	References	Location of Element in Each Reference
93. The method of claim 3 wherein said fluid is tolerant to contaminants, wherein said contaminants comprise drill cuttings from said drilling.	(A)	p. 1 cols. 1-2; p. 2 cols. 1-2; Figs. 4-6
	(I)	p. 30 l. 3 to p. 31 l. 8
	(L)	p. 1 col. 2
	(O)	p. 1 col. 1; p. 3 col. 1
	(P)	p. 1
	(Q)	HAL_0015055; See Reference (A) above
	(R)	p. 13 ll. 1-5; p. 14 (table 1); pp. 16-19 (tables 2, 4, 6, 9)

Asserted Claim 94
(depends from Asserted Claim 3)

Element	References	Location of Element in Each Reference
94. The method of claim 3 wherein said fluid does not exhibit sag when at rest.	(B) (G) (L) (M)	RM-63 brochure p. 1 p. 4 col. 1 p. 1 col. 2; p. 3 col. 2; p. 6 cols. 1-2 p. 1 col. 1; p. 4 cols. 1-2; p. 5 col. 2; p. 6 cols. 1-2

Asserted Claim 95
(depends from Asserted Claim 3)

Element	References	Location of Element in Each Reference
95. The method of claim 3 wherein said drilling fluid is substantially free of organophilic clay.	(B) (N) (O) (Q) (R)	Petrofree brochure p. 6; RM-63 brochure p. 1 p. 2 col. 2; p. 5 col. 2 p. 2 cols. 1-2; p. 3 col. 1; p. 9 HAL_0015053-55; See Reference (A) above p. 11 ll. 12-14

Asserted Claim 96
(depends from Asserted Claim 3)

Element	References	Location of Element in Each Reference
96. The method of claim 3 wherein said drilling is conducted without significant loss of drilling fluid.	(J) (L) (N)	p. 2 ll. 23-24; p. 8 ll. 7-10 p. 3 at col. 2 ll. 23-26 p. 5 at col. 2 ll. 7-29

Asserted Claim 97
(depends from Asserted Claim 3)

Element	References	Location of Element in Each Reference
97. The method of claim 3 wherein said drilling fluid does not require organophilic clays to provide filtration control.	(B) (N) (O) (Q) (R)	Petrofree brochure p. 6; RM-63 brochure p. 1 p. 2 col. 2; p. 5 col. 2 p. 2 cols. 1-2; p. 3 col. 1; p. 9 HAL_0015053-55; See Reference (A) above p. 11 ll. 12-14

Asserted Claim 98
(depends from Asserted Claim 3)

Element	References	Location of Element in Each Reference
98. The method of claim 3 wherein said drilling fluid demonstrates lower differences in surface and downhole equivalent circulating densities at faster drilling rates.	(B)	p. 3, 7

Asserted Claim 108

(depends from Asserted Claim 3)

Element	References	Location of Element in Each Reference
108. The method of claim 3 wherein said drilling fluid is ester-free.	(A) (H) (M) (N)	Figs. 15-16; p. 1 col. 2; p. 2 col. 2 pp. 3-6 p. 1 col. 2 to p. 2 col. 1 p. 2 col. 2 to p. 3, col. 1, pp. 8-12

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